

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) XXXXXX 05-04-2010		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Oct-2006 - 31-Dec-2009	
4. TITLE AND SUBTITLE Final Report for Development of a Portable Chlorine Dioxide Generator			5a. CONTRACT NUMBER W911NF-06-1-0502		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 206023		
6. AUTHORS David E Richardson			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Florida Board Of Trustees Office Of Sponsored Program University Of Florida Gainesville, FL 32611 -				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 51906-CH.1	
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT We have carried out research and development on a concept that can be used to produce a portable ClO2 generator that requires no power source. Our results after completion of the work indicate that this technology can be engineered readily to provide a wide range of desirable ClO2 concentrations, precursor formulations, and flow rates. The chemistry and chemical kinetics in our system are now well understood at a level that can allow initial prediction of performance under various conditions. The concepts have been demonstrated successfully with					
15. SUBJECT TERMS chlorine dioxide, generator, decontamination					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON David Richardson
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 352-392-6736

ARO W911NF0610502: Development of a Portable Binary Chlorine Dioxide Generator for Decontamination (Proposal 51906CH)

**DTRA BB06DEC053: Non-Electric Portable/Low Cost ClO₂ Generator for Surface Decon
FINAL Report (March 2010)**

PI: D. E. Richardson, University of Florida

1. Introduction

We have carried out research and development on a concept that can be used to produce a portable ClO₂ generator that requires no power source. Our results indicate that this technology can be engineered readily to provide a wide range of desirable ClO₂ concentrations, precursor formulations, and flow rates. The chemistry and chemical kinetics in our system are now well understood at a level that can allow initial prediction of performance under various conditions. The concepts have been demonstrated successfully with prototype devices and materials. The major goals of this work were to optimize the chemistry, develop formulations with additives, and ultimately choose the best candidates for production of a device.

Our concept relies on the use of flow-through spherical bead resins that are brought in contact with a precursor solution only at the time of desired ClO₂ release. All of the preparative chemistry for ClO₂ is based on oxidation-reduction reactions, and the UF approach separates the reductive and oxidative components to allow for stable long term storage in a binary sprayer or other device. Unlike approaches in which two liquids (reductant and oxidant solutions) are mixed (dual chamber sprayers) or a solid reactant is dissolved into a liquid, the interaction of the two reactants relies instead on the well established principles of liquid flow through a resin bed. The physical flow and reactivity characteristics of this process are very well understood in view of its long history in water purification and treatment. In particular, the high surface area of the resin allows for simple “instantaneous” mixing of the solid reactant with the liquid component, in contrast to the slow dissolution of solids or the complicated mixing of two liquids. This technology is therefore adaptable to devices that must release ClO₂ upon demand. The general concept is shown below in Figure 1.

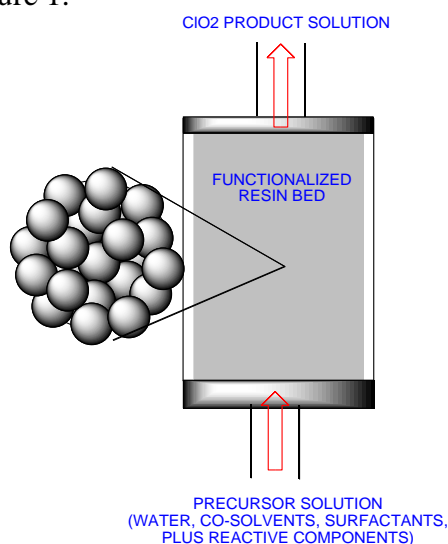


Figure 1. Basic concept for a liquid-resin device for ClO₂ production.

The UF approach is notable in part for the unique materials that can be employed. The resins can be as simple as commercial ion-exchange beads or more customized materials such as functionalized, covalently modified beads. We set as an initial goal to produce a prototype device that can deliver 1 L of reactive solution in < 1 min with $[\text{ClO}_2] > 10 \text{ mM}$. This goal has been easily achieved.

2. Highlights

Some highlights from the detailed final report that follows are given here.

- (1) Trihalide ion exchange resins are readily prepared and are highly active for conversion of chlorite to ClO_2 . The resins are moderately stable under extreme conditions (activity retained for 40 days at 75°C), are very stable to long term storage at room temperature, and are safe to handle.
- (2) With moderate flow rates, conversion yields of dilute aqueous chlorite solutions (< 50 mM) in the 40-50% range can be achieved with low volumes of resin. Conversions for more concentrated solutions (up to 200 mM) decline to about 20%.
- (3) Addition of polar cosolvents such as acetone, ethanol, etc., drastically increases conversion efficiencies under the same conditions, with yields as high as 75%.
- (4) Triton (5 mM) increases conversion efficiency to ~75%.
- (5) A detailed kinetic model can be used to model effluent yields as a function of flow rates and feed concentrations. The analysis shows that bromine release by the resin becomes rate limiting only at higher chlorite concentrations (>100 mM).
- (6) A functioning prototype has been tested and shows that laboratory observations are reflected in practical use.
- (7) We have developed a detailed kinetic model and improved experimental protocols that show the behavior of the tribromide/ bromine resin is not at equilibrium, thereby limiting the ultimate utility of the method at very high flow rates. However, the conversions can still be high with moderate flow rates, producing “high test” ClO_2 with concentrations >5000 ppm.
- (8) The full capacity of tribromide resins has been demonstrated with slow flow production studies.
- (9) Some simple kinetic studies on CEES have been done as a stimulant to prepare for HD agent studies.
- (10) Benchtop generators based on COTS glassware have been assembled and tested for optimal production of ClO_2 at high concentrations.

(11) 100% methanol provides the highest concentration of ClO_2 from the gravity fed generator, and mixed methanol/ water solvent can be used to modify the level and efficiency.

(12) The role of resin bed geometry has been explored in order to characterize the operation of the generator.

(13) Ion chromatography has been used to determine ion products in the generator solutions. Residual chlorite in particular is an important component of the generator solutions. Variations in product ion levels for different preparations, especially in initial effluents, have been traced to the preparation of the resin, and a more consistent preparation has been devised that leads to highly reproducible generation.

(14) Agent studies were conducted by Battelle Labs and showed that high test ClO_2 has rapid decon capability and high capacity when the formulation is supplemented with high concentrations of chlorite. The activity exceeds that of the bleach control.

3. Results for Tasks

Task 1: The production of stable resin products that can be used in the cartridge spray devices

General. There are a number of resin types that were considered for this project, including commercial ion exchange resins and some commercial oxidant resins. Based on the work to date, we strongly prefer oxidant resins prepared from COTS ion exchange resins. In this approach, chlorite is dissolved in the precursor solution. An alternative approach in which chlorite is bound to anion exchange resins does work as expected using, e.g., bromine water as the liquid component. However, we have not found a dry chlorite resin that is stable, and the wet resins also decay rapidly and would be unsuitable for a device. Although other oxidant resins have been considered and in some cases produced, in work to date **trihalide resins** are by far the most stable, conveniently produced, and reactive toward chlorite solutions.

Specific Results for Task 1

Resin Preparation. We have investigated various commercial ion-exchange resins for their applicability in the envisioned devices. Parameters that can be varied include stability to halogen oxidation, hardness, spherical uniformity and size, etc. In addition we have investigated other polymeric ion-exchange polymers found in less common products.

The following resins have been prepared from commercial Cl^- or OH^- forms and studied extensively.

(1) Rohm and Haas Amberlite IRA-900 (16-50 mesh) trihalide forms:

stable and active for ClO_2 production: Br_3^- , Cl_2Br^- , Br_2Cl^-

unstable but active for ClO_2 production: Cl_2I^- (oxidation of iodide)

stable but not active for ClO_2 production: I_3^- , Br_2I^-

(2) Dowex Marathon A (30-40 mesh): stable and active Br_3^- , Br_2Cl^-

Examples - Preparation of Br_3^- resins. Amberlite™ anion exchange resin in the OH^- form was converted to the Cl^- form with dilute hydrochloric acid then to the Br^- form using NaBr . All free Cl^- and Br^- ions were washed from the resin. Saturated aqueous bromine at 0.20 M was diluted to 10 mM and slowly rinsed the column until the resin was dark red with significant amounts of Br_2 in the effluent. Shaking Br_2 with the Br^- form of resin in a separatory funnel achieved the same result. The resin was then washed with water until the Br_2 content of the effluent was at a minimum. In other experiments, Dowex™ Marathon A resin in the Cl^- form was converted to the red tribromide resin by the same method. The tribromide resins are stable in the dry and wet forms (Figure 2).



Figure 2. A sample of Marathon A tribromide resin is shown.

Capacity of resin for Br_3^- . To determine trihalide equivalents in the modified resins, the trihalide was reduced by passing a standard stoichiometric excess of L-ascorbic acid in 0.10 M HCl slowly through column until all traces of red color were replaced by light yellow. The unreacted L-ascorbic acid in the effluent was standardized iodometrically to determine resin capacity.

The capacity of the resin for Dowex Marathon A Br_3^- was experimentally determined to be 1.88 ± 0.02 mmol/mL of wet un-compacted resin. When corrected for the volume change (tribromide resin is much more compact than chloride form), this is ~96 % of the literature value of 1.4 mmol / mL binding sites (wet basis) in the Cl^- form. The dry Dowex Marathon A Br_3^- resin (dessicator stored) contains 1.58 mmol/g resin. Amberlite IRA900 Br_3^- contains 3.49 mmol/g as dry resin, and Marathon A Br_2Cl^- contains 1.48 mmol/g as dry resin.

Full capacity chlorite flow study. Figure 3 illustrates a study designed to show the production level of ClO_2 using the full capacity of a tribromide resin. Through the run the pH remains stable in the 6-7 range. The maximum conversion is ~58% on average until the capacity of the resin is nearly exhausted. The total production is ~0.045 mol of ClO_2 , somewhat lower than the theoretical yield based on the tribromide loading determined above.

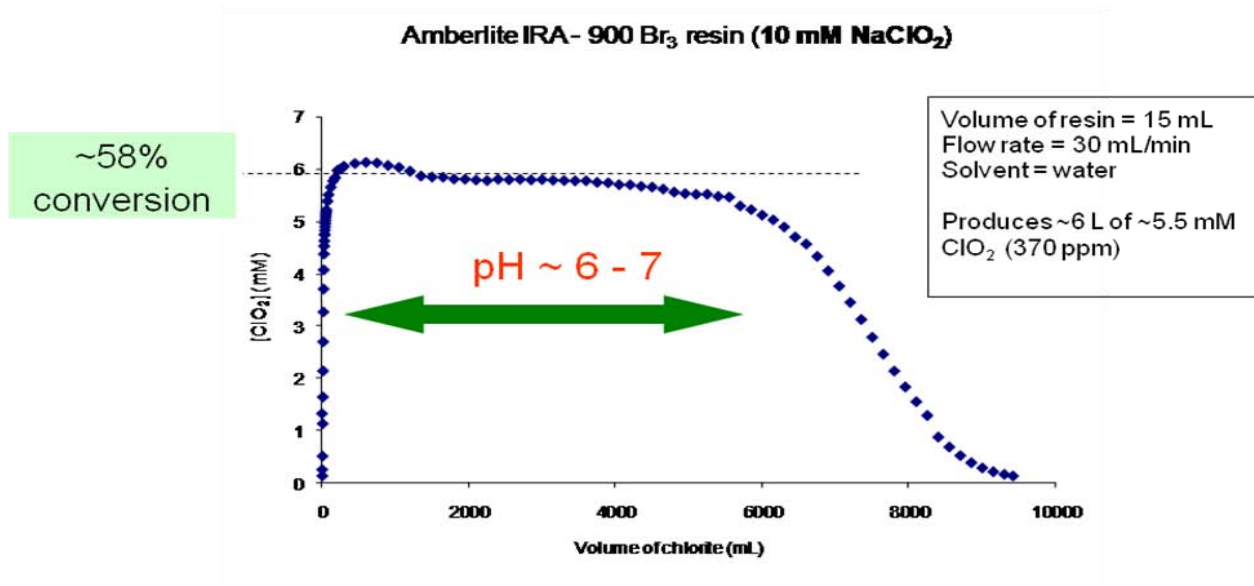
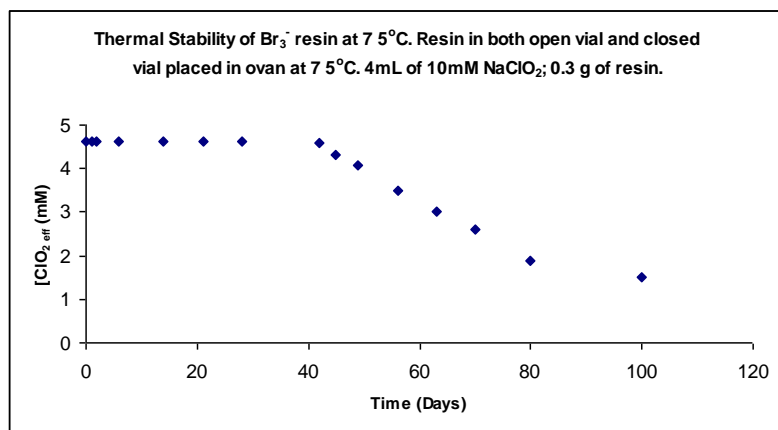
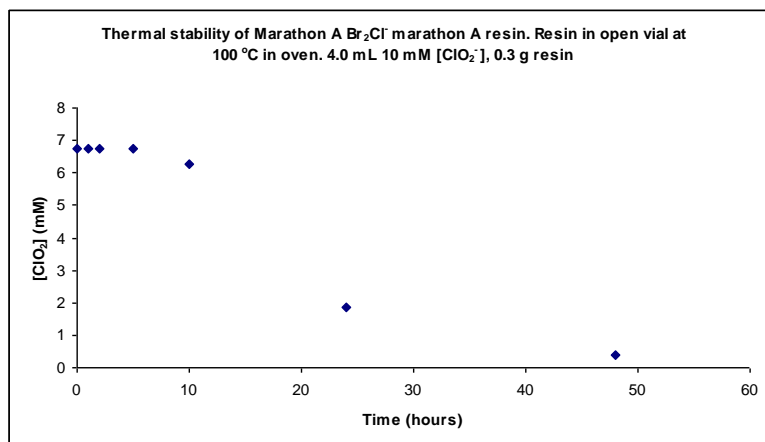
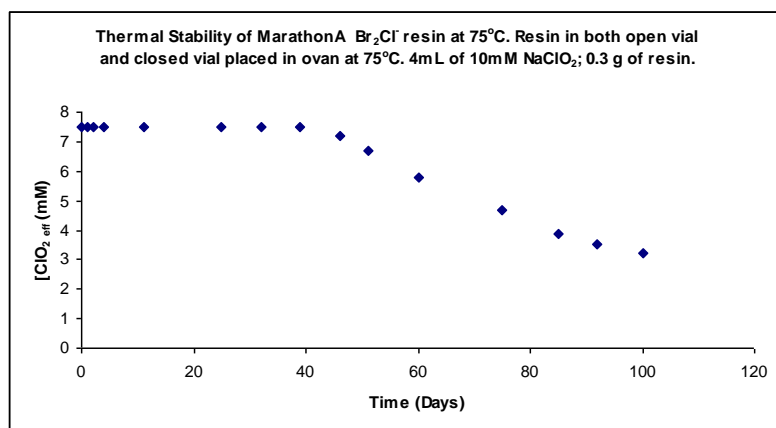
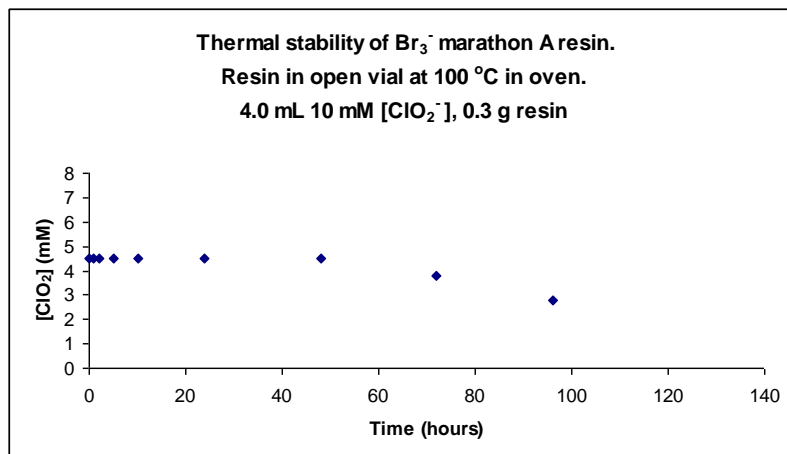


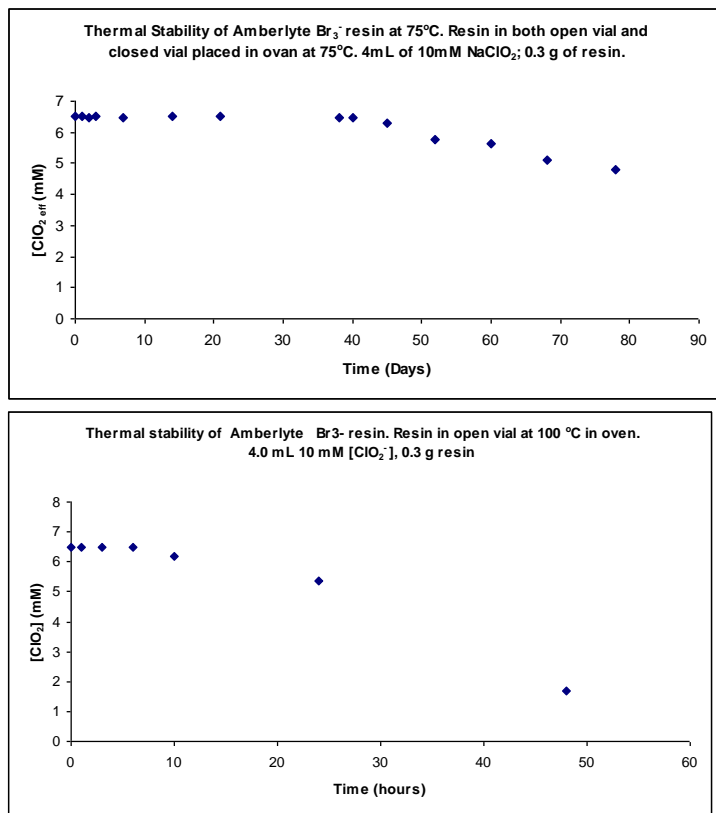
Figure 3. Production of ClO₂ by tribromide resin with constant precursor flow (0.1 M chlorite) until exhaustion of capacity. Resin volume is 15 mL.

Safety. The tribromide resin is stable in dry form at room temperature and above (see below) and the resin is much easier to handle than pure or aqueous bromine. Accidental spillage of the resin will not release free bromine at toxic levels.

Thermal stability. This was assessed by placing the resins in open vials in a 75 C or 100 C oven for many days. The resin was then shaken with a standard chlorite solution to determine reactivity for production of ClO₂. The results show that the resins even under these extreme conditions retain significant reactivity. At constant 75 C (167 F), the resin is stable for 40 days before appreciable loss of activity is observed. Storing the resins in closed containers at lower temperatures (below 75 C) results in very long storage times. Room temperature storage retains 99% activity for at least a year. See charts below for 75 C and 100 C experiments.







In other experiments, the resins were subjected to much higher temperatures on a melting point apparatus. Color change was noted only at high temperatures of 190 C or more. See sequence below in Figure 4.

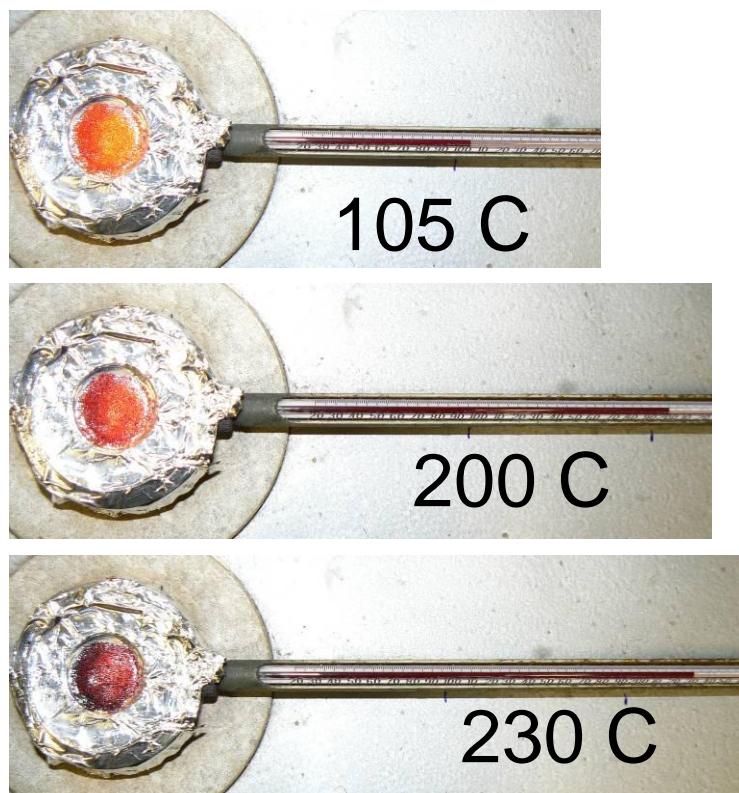


Figure 4. Decomposition of tribromide resin occurs at temperatures >190 C.

Trihalide resin preconditioning. From stirred batch reactor studies, we have found that COTS ion exchange resins have a small concentration of sites that undergo a relatively rapid (timescale minutes) reaction with ClO_2 . Once treated with dilute ClO_2 the resins react only slowly with additional ClO_2 . Our flow studies described below are not affected by the rapid reaction since the ClO_2 residence time on the resin bed is short (seconds) and the resins are essentially preconditioned during the experiments. However, we recommend that preconditioned resins are used in one-shot reactors for applications requiring high yields.

Preparation of Metal Oxidant Resins A second class of redox resins has been investigated in which strong transition metal oxidants are bound to ion exchange resins. In the prototype we produced, $[\text{Fe}^{\text{III}}(\text{phen})_3]^{3+}$ was bound to a large pore cation exchange resin (Amberlyst) producing dark blue spheres with active Fe(III) (blue solution of complex in left cuvette, Fe(II) form on right). See Figure 5.

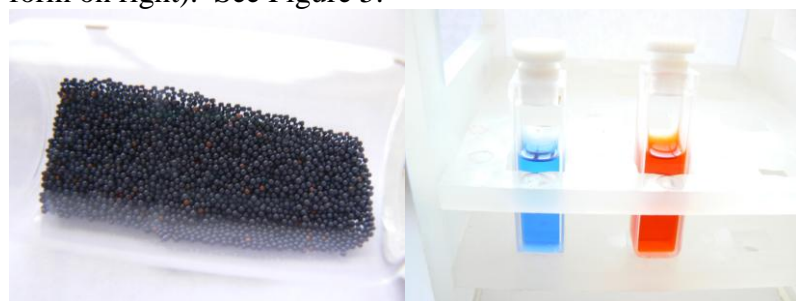


Figure 5. Fe(III) –Amberlyst resins and solutions of $[\text{Fe}^{\text{III}}(\text{phen})_3]^{3+}$ (left) and $[\text{Fe}^{\text{III}}(\text{phen})_3]^{2+}$

Although redox active, the Fe(III)-resin is not readily used in practical chlorite reduction because the complex is unstable in neutral pH solutions, and decomposition of the complex in the resin bed competes with oxidation of chlorite. We have investigated other chlorite sources that can be used in non-aqueous solvents, but the choices are limited by solid state instability of many chlorite salts that have non-aqueous solubility. There is an indication that methanolic solutions can be used, but modifications and potential efficacy would be limited.

These observations led us to focus on the trihalide redox resins, which can be used with a vast selection of co-solvents and additives.

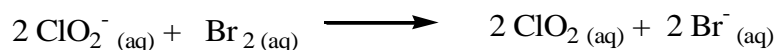
Task 2: Development of precursor solution component formulations to achieve desirable levels of ClO₂ production

General. Our studies have shown that the overall kinetics of these liquid-resin reactors can be understood quantitatively, allowing prediction of yield of ClO₂ as a function of trihalide resin type, flow rate, chlorite concentration and bed volume. The resin capacities and physical properties of the solutions can influence the kinetics significantly, so we focused on the appropriate design parameters needed to produce desirable reaction product distributions.

For example, precursor solution residence time (= volume/flow rate) in the reactor cartridge is an important parameter in determining ClO₂ yield. High yields are achieved with tribromide resins with longer residence times, and the flow rates are acceptable for a design that would deliver ClO₂ solutions on the order of 1 min.

Specific Results for Task 2

Tribromide resins. The primary reaction used for the production of ClO₂ in our work involves the oxidation of a ClO₂⁻ salt with aqueous bromine as shown below.



The kinetic parameters of this reaction have been reported for aqueous solution, and the reaction is rapid over a wide pH range (1 – 8).

Of course, bromine itself cannot be resin bound. On the other hand, tribromide ion, whether in solution or resin bound, is in labile equilibrium with bromine according to:



The K_{eq} value for this equilibrium is ~0.05 in aqueous solution. When the anions are resin bound, the K_{eq} value is lower (<0.001), presumably as a consequence of the higher affinity of tribromide for the resin compared to bromide. The tribromide resin therefore serves as a *solid state source* of Br₂, and in fact the resin is a more concentrated form of bromine than saturated bromine water (the resins we have prepared are 20 -40% Br₂ by weight). Passage of chlorite solution through

the resin produces ClO_2 , and the free bromine consumed is replenished via the tribromide/bromine equilibrium reaction. (Figure 6)

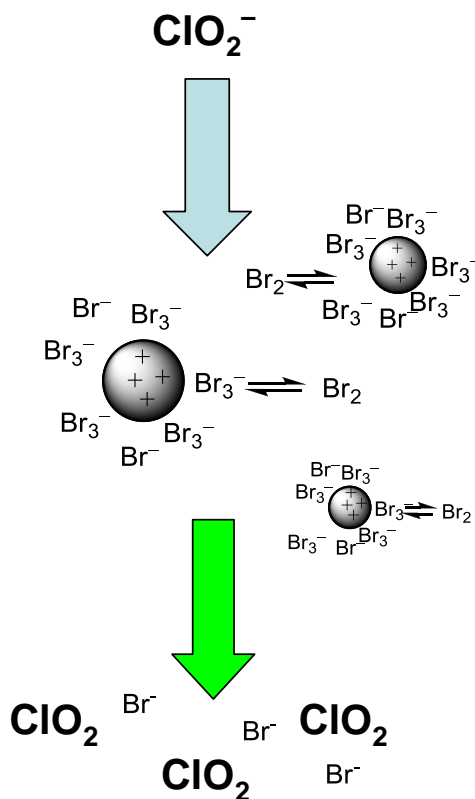


Figure 6. Resin-bound tribromide is in equilibrium with free bromine. Free bromine reacts with chlorite in the precursor solution, producing bound bromide and chlorine dioxide. Release of additional bromine is facile for oxidation of further chlorite in the flowing precursor solution

Our experiments produce ClO_2 in the pH range 6-8 with no trace of Br_2 in the effluent, a clear advantage for producing less corrosive decon solutions (aqueous bromine releases HBr).

Consistency of ClO_2 production. We have shown that the concentration of ClO_2 produced by a redox resin flow experiment does not vary with time (i.e., the concentration is the same in an initial aliquot as in the final aliquot when the output is fractionated). All experiments are run with a large excess of bromine capacity in the resin bed.

Conversion studies (low concentration chlorite feeds (<50 mM)). The conversion of ClO_2^- in the feed to ClO_2 by Br_3^- resin was studied with respect to $[\text{ClO}_2^-]_{\text{feed}}$ as well as flow rate through column. The $[\text{ClO}_2]$ in the effluent is constant provided the $[\text{ClO}_2^-]$ in the feed and the flow rate are fixed. The ClO_2 yield increases linearly with increasing $[\text{ClO}_2^-]_{\text{feed}}$ (Figure 7).

The conversion of ClO_2^- is also dependent on the rate at which it flows through the column. The maximum conversion with flow rates we have studied is ~50%. Flow rate is an indirect measure of the contact time between the reactants. The column can be modeled as a tubular reactor where there is axial but no radial variation in concentration (Figure 8). Under the conditions used (dilute chlorite), pseudo-first order conditions can be imposed since Br_2 is in large molar excess

and in rapid equilibrium with Br_3^- on the resin. However, the limits of observed conversions suggest that much of the column is not at equilibrium due to mass transport limits (see below).

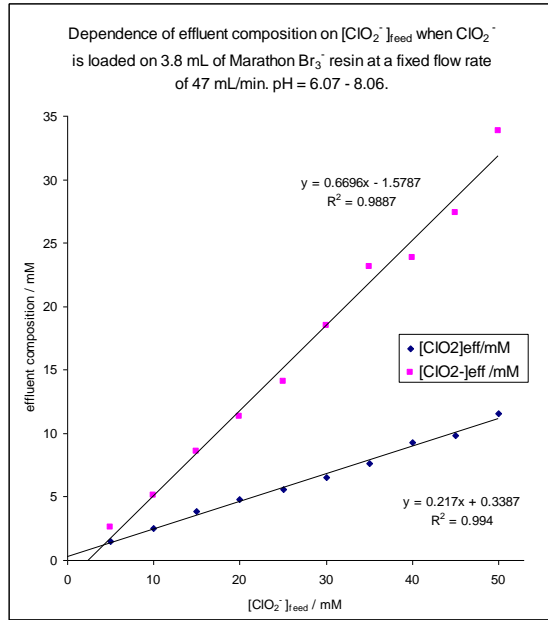


Figure 7. Typical dependence of chlorine dioxide yield and residual chlorite on the chlorite feed concentration. Conditions noted on figure.

An equation that relates all the variables involved is shown below (see also Figure 8).

$$\frac{1}{v} = \frac{1}{k_{\text{obs}} V} \ln \left(\frac{[\text{ClO}_2]_{\text{max}}}{[\text{ClO}_2]_{\text{max}} - [\text{ClO}_2]_{\text{eff}}} \right) \quad (1)$$

where

v = volumetric flow rate

V = volume of resin bed

k_{obs} = pseudo-first order rate constant

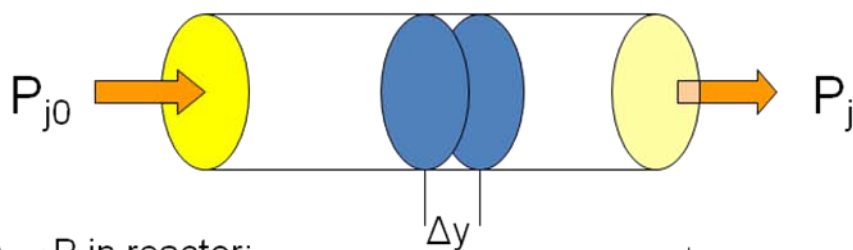
$[\text{ClO}_2]_{\text{max}} = C_{\text{max}}[\text{ClO}_2^-]_{\text{feed}}$ = maximum concentration of chlorine dioxide generated from an infinite volume bed with flow rate approaching zero

$[\text{ClO}_2]_{\text{eff}}$ = concentration of chlorine dioxide in effluent

Experimental data produce acceptable fits to this equation as shown in Fig 9A. Alternatively, the data can be fit by using non-linear regression based on the equation below for product concentration as a function of flow rate (Figure 9B).

$$[\text{ClO}_2]_{\text{eff}} = C_{\text{max}} [\text{ClO}_2^-]_{\text{feed}} \left\{ 1 - \exp \left(- \frac{V k_{\text{obs}}}{v} \right) \right\} \quad (2)$$

The resulting parameters are consistent for different resins and conditions, and they are presented in Table 1. In these fits, we have not determined the void volume of the bed and simply use the total bed volume for V .



For $A \rightarrow B$ in reactor:

$$B_{\text{eff}} = B_{\text{max}} (1 - e^{-kV/v})$$

where

B_{eff} = Concentration of B in effluent

B_{max} = Max concentration of B (slow flow)

k = first order rate constant for $A \rightarrow B$

V = Volume of tube

v = flow rate

V/v = residence time = t_R

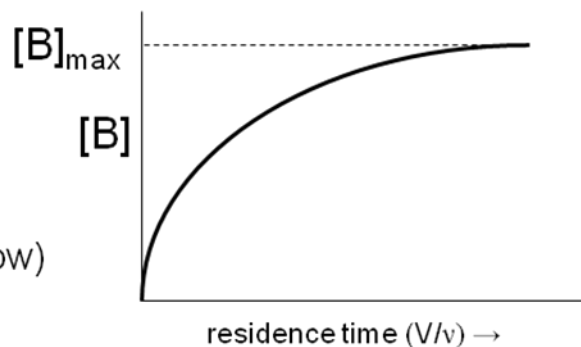


Figure 8. Basic kinetic equation and parameters for a plug flow reactor. (right) Production of product B as a function of residence time of the plug in the reactor. The basic kinetic model is independent of shape of the reactor and only depends on volume and flow rate.

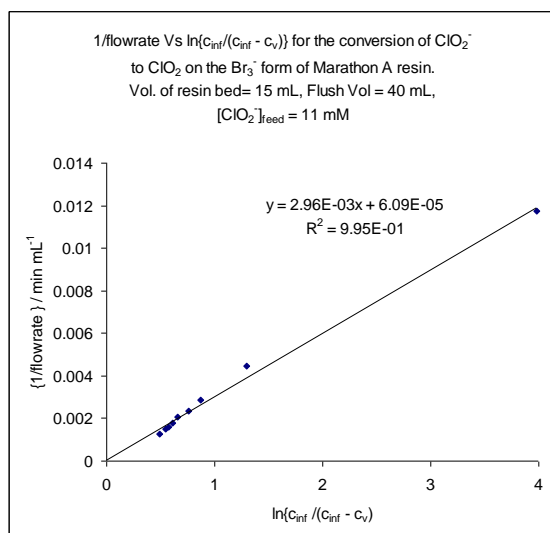


Figure 9A.

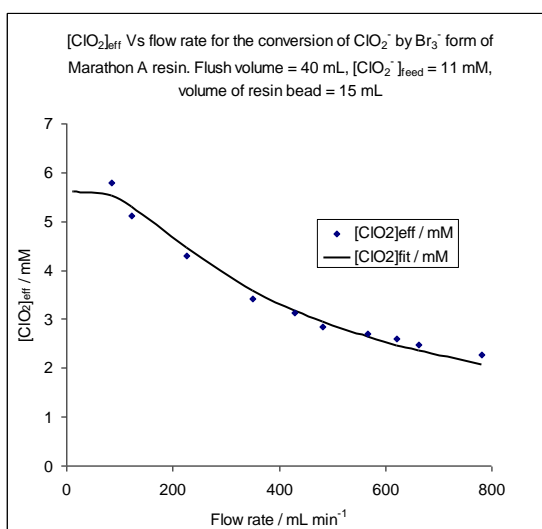


Figure 9B.

Table 1. Pseudo first-order rate constants and maximum conversions at different concentrations of feed.

$[\text{ClO}_2]_{\text{feed}} / \text{mM}$	$[\text{ClO}_2]_{\text{max}} / \text{mM}$	Maximum conversion %	$k_{\text{obs}} V / \text{mL (min)}^{-1}$	$k_{\text{obs}} / (\text{min})^{-1}$	Resin type
22	11	50	385	26 ± 1	Amberlite
33	13	40	397	27 ± 2	Amberlite
11	5.6	50	349	23 ± 1	Marathon

The kinetic parameters of this resin-liquid system are consistent with the known rate of reaction of Br_2 with ClO_2^- . Using rate constants from Toth and Fabian and our measured concentration of Br_2 in equilibrium with the resin ($\sim 0.3 \text{ mM}$), we would estimate k_{obs} should be in the range of 50 min^{-1} , which compares favorably with the experimental value ($\sim 60 \text{ min}^{-1}$) after accounting for the estimated void volume in the resin.

Modeling ClO_2 yields with concentrated chlorite solutions - a complete kinetic model for ClO_2 production in tubular flow trihalide resin devices. Experiments showed that ClO_2 solutions on the order of 10 mM are produced readily from dilute chlorite solutions, but the yields do not vary linearly with increasing chlorite concentrations in the $> 50 \text{ mM}$ range as predicted by the PFR model, and indeed the kinetics became distinctly non-ideal in this range (Figure 10). Therefore, we undertook a more thorough examination of the kinetics of chlorite conversion and ClO_2 yields as a function of chlorite concentration and residence time (resin bed void volume/flow rate). The tribromide resins were investigated, as was the more reactive Amberlite IRA900 ClBr_2^- resin.

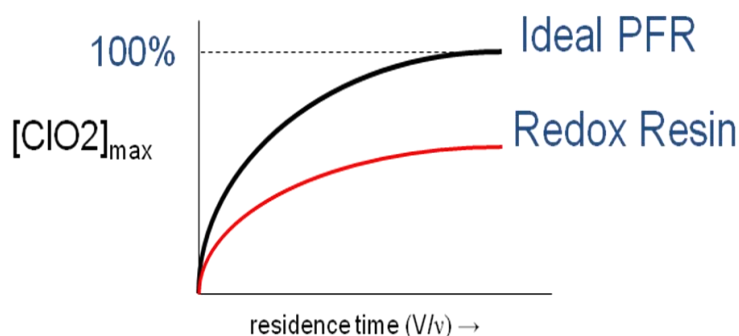


Figure 10. Actual performance of redox resin does not follow ideal plug flow reactor kinetics. At high concentrations of chlorite, the ultimate conversions are increasingly lower than predicted

The first goal was to refine the kinetic measurements by sampling consistent fractions from the column apparatus *after the flowing reactor has reached steady state production*. Early studies

captured all of the precursor solution as it emerged from the reactor, causing some variation in the results due to the initial front of the precursor solution. See Figures 11 and 12 for examples.

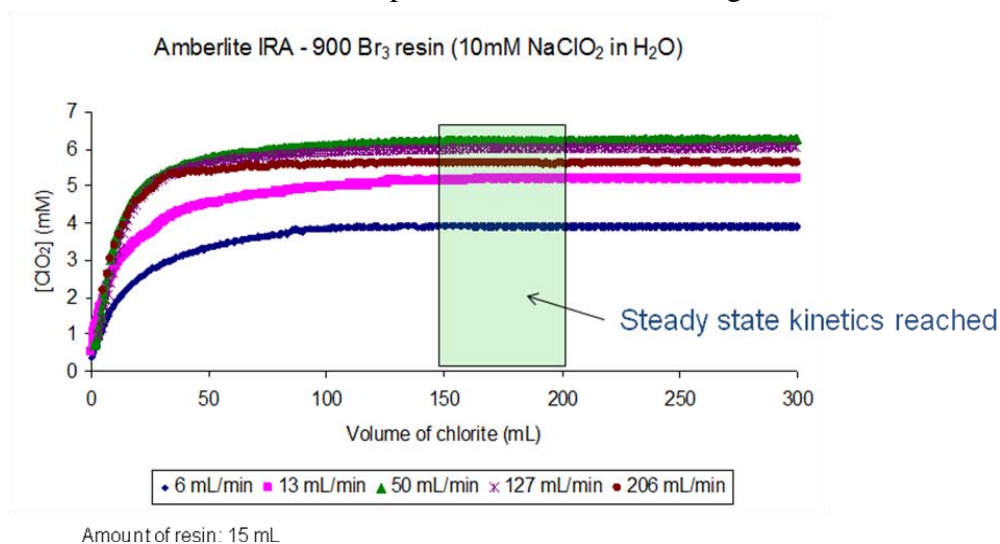


Figure 11. Illustration of the fraction captured for kinetic studies. Here between 150 and 200 mL of precursor flow.

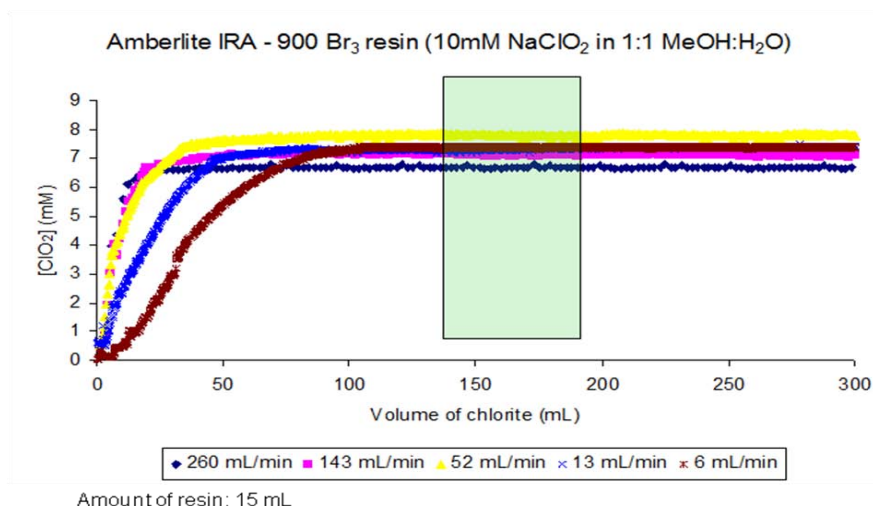


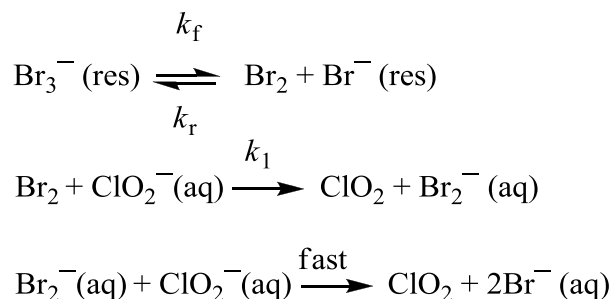
Figure 12. Illustration of the fraction captured for kinetic studies. Note the variation in the first 50 mL depending on flow rate that occurs with methanol cosolvent. It is important to capture a later fraction once a steady state has been reached.

There are various reasons why steady state ClO₂ yields will not vary linearly with chlorite feed concentration as predicted by the PFR model. We considered two dominant factors. First, kinetic saturation can occur if the chlorite concentration is so high that bromine production by the resin is insufficiently rapid to maintain equilibrium concentrations of bromine in the liquid phase.

Second, there may be mass transport effects due to liquid flow through the resin bed since bromine is released into the flowing solution, and the reactant concentrations may not be homogeneous as a result. The latter was incorporated into the simple model above by inclusion of a $[\text{ClO}_2]_{\text{max}}$ term ($= C_{\text{max}}[\text{ClO}_2^-]_{\text{feed}}$), which was found empirically to be about 40- 50% of the stoichiometric maximum (100% conversion of chlorite) under the best conditions.

The following mechanism is used to derive a more general kinetic model:

Scheme 1



In the first reversible step, bromine is released from the resin, leaving the trihalide site occupied by bromide. In solution this equilibrium favors tribromide with $K_{\text{eq}} = 0.05 \text{ M}$. We determined in stirred suspensions that for the resins $K_{\text{eq}} < 10^{-3} \text{ M}$ as a result of the higher binding affinity of the resin for tribromide relative to bromide. The rate constant k_f in solution is very high but is significantly lower in the resin. In addition, k_f for the resin is expressed in M/s using the usual standard state convention for the solid resin.

The k_1 reaction is the rate determining homogeneous one-electron oxidation of chlorite by bromine, producing ClO_2 and the dibromine radical anion. The rate constant for this reaction is known in solution, and we have used a value of $1300 \text{ M}^{-1} \text{ s}^{-1}$ in all models. The fast ($k > 10^6 \text{ M}^{-1} \text{ s}^{-1}$) third reaction produces bromide and a second equivalent of ClO_2 .

Note that the following reaction also occurs for aqueous bromine:

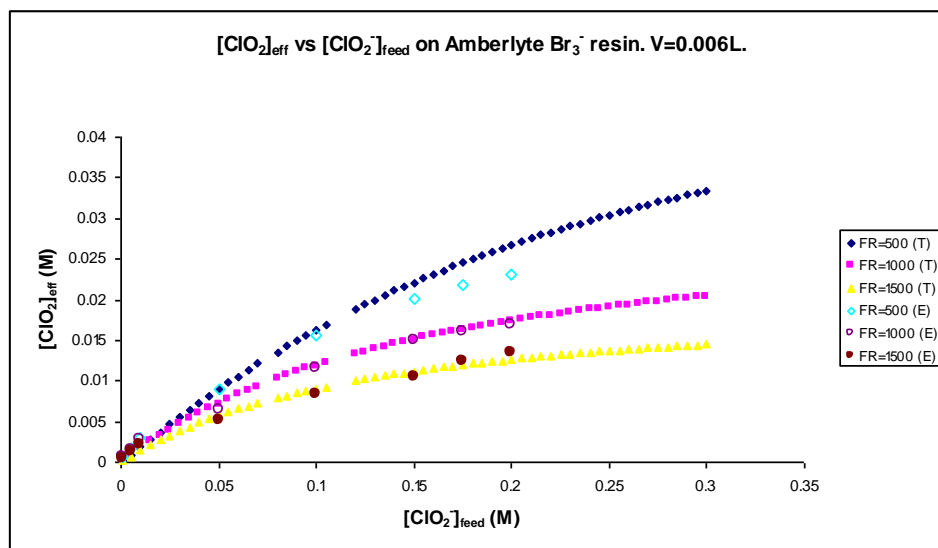
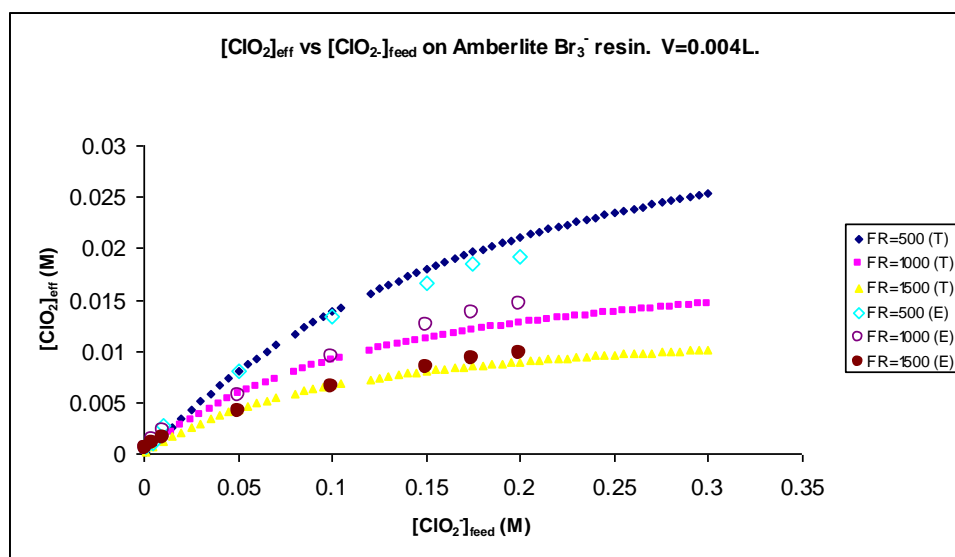


This reaction produces acid in static bromine solutions. In the flow reactor, this reaction does not compete with step 2 in Scheme 1, and as a result the effluent from the flow reactor is pH neutral (i.e., virtually all bromine is reduced by chlorite).

The mechanism of Scheme 1 can be used to derive the following flow reactor rate law via the steady state approximation.

$$[\text{ClO}_2]_{\text{eff}} = C_{\text{max}} [\text{ClO}_2^-]_{\text{feed}} \left\{ 1 - \exp \left(- \frac{2k_1 k_f}{(k_r + k_1 [\text{ClO}_2^-])} \left(\frac{V}{v} \right) \right) \right\}$$

The factor C_{\max} defines the maximum conversion that can be achieved given the other determinants of reactor efficiency. The volume V in fits to is set as the void volume of the resin bed (determined by “titration” of dry resin with water until saturation.) When $kr \gg k_1[\text{ClO}_2^-]$ (i.e., low chlorite concentrations) a linear dependence on $[\text{ClO}_2^-]$ is predicted as observed (see above). However, when $kr < k_1[\text{ClO}_2^-]$ saturation occurs and the conversion levels off at high $[\text{ClO}_2^-]$ values. Typical fits are shown below.



Although general kinetic behavior is consistent with the above equation (e.g., saturation at high chlorite concentration), over a wide range of flow rate and chlorite concentration the fit is not good. We therefore sought an improved model and focused on the idea that some or much of the column was not at equilibrium with respect to the first equation in Scheme 1 above (bromine release).

A careful study of the effect of added bromide ion in the precursor solution gave us quantitative insight into the non-equilibrium nature of the bromine equilibrium. As seen in Figure 13, added bromide significantly, but not completely, inhibits the product (ClO_2) yield at all flow rates. If the bromine concentration was at equilibrium, then bromide addition *would have no effect*. This is because the equilibrium equation in Scheme 1 must be true locally and the addition of bromide (which reacts with free bromine to produce tribromide in solution) would simply shift the equilibrium to maintain the required Br_2 concentration according to the first equation in Scheme 1. The observed effect has two consequences. Most importantly, it shows that Br_2 is not uniformly distributed in the flowing column and therefore is less concentrated in some volume regions than others. Second, since bromide is a product of the reaction with chlorite (Scheme 1), the reaction is *self inhibiting*.

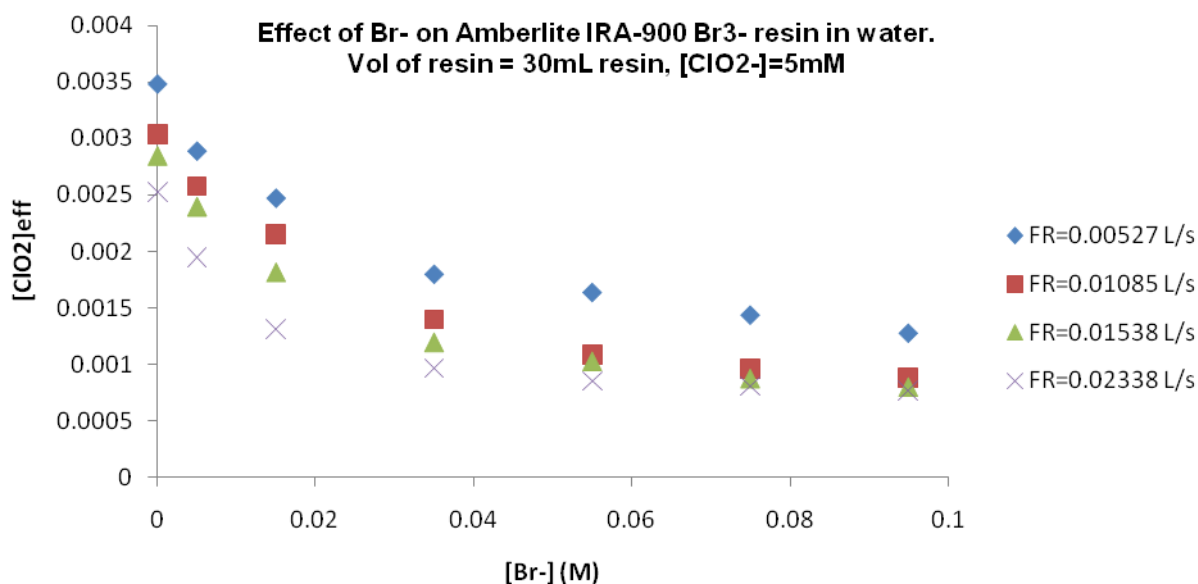
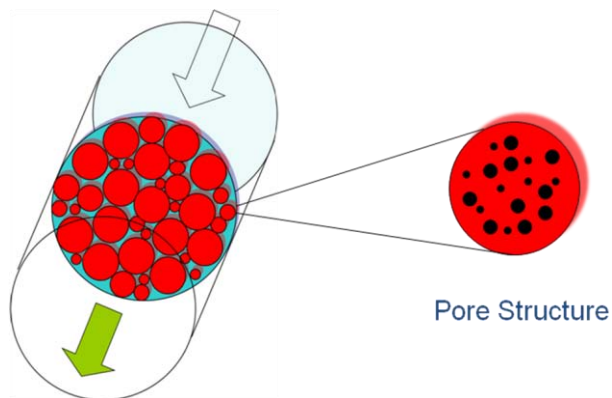
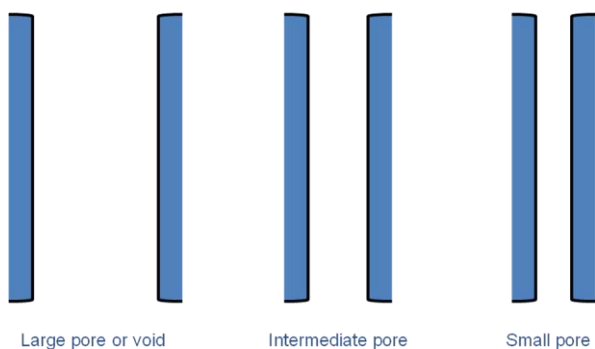


Figure 13. Effect of added bromide in the precursor solution on ClO_2 yields.

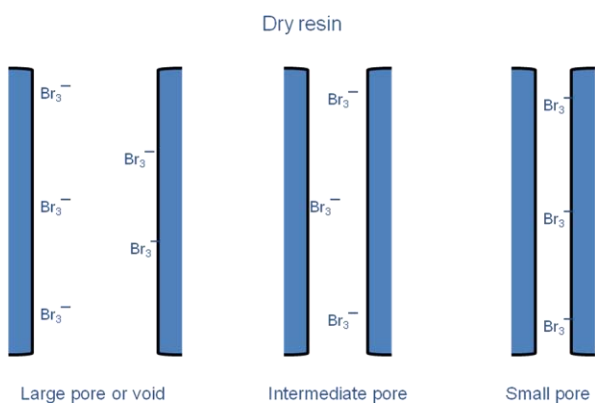
We can understand this result from the following simple model for the resin bed. Consider a slice of the bed:



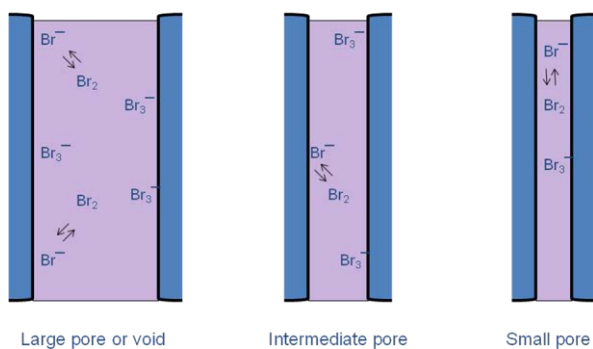
The slice has many pores running through it. Some are quite large and include the spaces between the beads. Others are moderate in size and pass through the beads, and yet others are quite narrow through the beads:



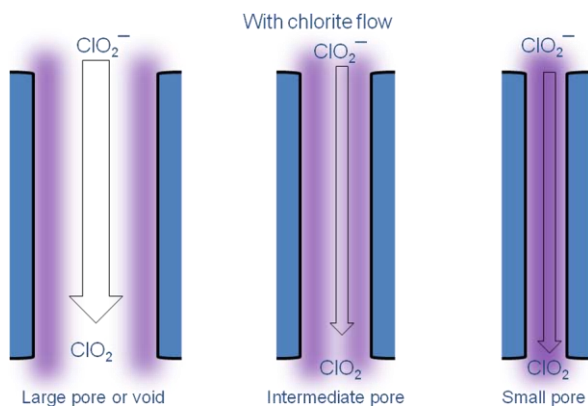
In the dry resin, tribromide is bound to the walls of these pores and the surface of the beads:



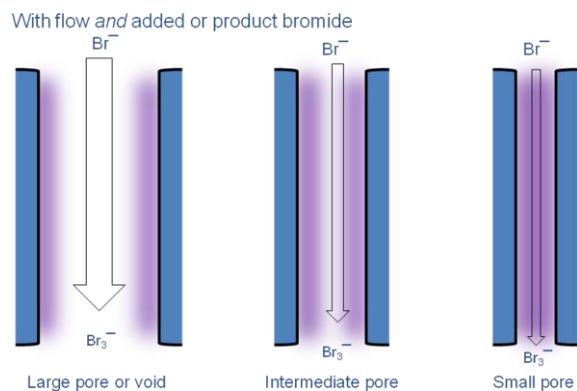
In wet resin (no flow), the bromine concentration in the pores will come to the same concentration as demanded by the equilibrium reaction constant (~ 0.001):



When chlorite flow is started, bromine in the largest pores is rapidly depleted. *This is presumably the origin of the $C_{max} < 1$ result found empirically*, as there is a limitation to the bromine available due to the physical flow. In addition, at high chlorite concentrations the bromine is depleted to less than equilibrium concentration in all of the pores as described above:



Addition of bromide further depletes the bromine (through formation of aqueous tribromide in the pores). Release of bromine from the beads not sufficiently rapid to replenish the effects of flowing solution and added bromide in much of the reactor volume.



Additionally, bromide produced by the reaction itself will remove bromine. Only the smallest pores will maintain equilibrium concentration of bromine, and overall these effects will reduce ClO₂ yield to a significant extent.

The equation below summarizes these effects on the reactor yield and gives an excellent fit to a wide range of experimental conditions. The structure of the equation is rather simple. If there were no depletion by bromide in any pores, $a = 1$ and the inhibition would disappear. Since bromide does inhibit, $a < 1$. The above saturation effect from Scheme 1 is contained in the last term.

$$[\text{ClO}_2]_{\text{eff}} = C_{\text{max}}^0 \left[\underbrace{a + (1-a) \left(\frac{1}{1 + K([\text{Br}^-]_{\text{added}} + [\text{Br}^-]_{\text{prod}})} \right)}_{\text{Bromide inhibition}} \right] \underbrace{[\text{ClO}_2]_{\text{feed}} \left\{ 1 - \exp \left(- \frac{2k_1 k_r}{(k_r + k_1 [\text{ClO}_2^-])} \left(\frac{V}{v} \right) \right) \right\}}_{\text{Saturation effect}}$$

$[\text{ClO}_2]_{\text{eff}}$ = concentration of chlorine dioxide in effluent

v = volumetric flow rate

V = volume of resin bed

C_{max}^0 = maximum conversion to chlorine dioxide generated from an infinite volume equilibrated bed with flow rate approaching zero

a = fraction of bed volume in “small” pores

$(1-a)$ = fraction of bed volume that is non-equilibrated

Overall, this equation gives an outstanding fit to the results of 128 separate experiments:

$k_1 = 1300 \text{ M}^{-1} \text{ s}^{-1}$ (fixed – literature value)

$C_{\text{max}} = 0.62 \pm 0.05$

$a = 0.11$ (11% of bromine in “small” pores)

$K_{\text{pore}} = 40 \pm 10$ (lit = 19 in bulk)

$k_f = 0.16 \pm 0.01 \text{ M s}^{-1}$

$k_r = 229 \pm 30 \text{ s}^{-1}$

$R^2 = 0.9972$

An excellent check of the consistency is obtained from the bromide inhibition constant (K in the above equation). The derived bromine/tribromide equilibrium constant is essentially the same as that in aqueous solution (40 vs 19, with an error of about 25% on the fit). The k_f/k_r value (equivalent to the equilibrium constant for bromine release from the resin) is 7×10^{-4} , which is also in excellent agreement with independent measurements in wet resin.

Notably, the derived fraction $a = 0.11$, suggesting that only ~11% of the bromine-producing sites are always at equilibrium no matter how much bromide is present. This can be thought of as the

layer of solution close to the resin surface. About 60% of the resin bed volume is not available for reaction (C_{max}) due to physical flow in large spaces and perhaps other side reactions not yet identified. Thus the poor overall fit of the basic PFR model is explained. The reactor is highly *non-ideal*, but it remains more than sufficient to be used for production of practical concentrations of ClO_2 on demand.

Task 3: Investigation of additives in the precursor solutions that can improve efficacy for chemical and biological agents

General. Successful formulations for CBW agent decon are generally not single component, and usually additives (such as cosolvents and surfactants) are included that modify the solubility of agents, efficacy with biological agents, reactivity, and other physical properties (such as freezing point, stability, pH). It is important to determine the extent to which our liquid-resin binary design can be used with such additives.

We have focused on solvent composition and surfactant additives in this study, as these can make a large difference in the extent of contact of the decon solution with agents on surfaces.

Specific results for Task 3

Solvent composition study. In addition to the studies in water described above, we have also investigated several different co-solvent compositions. Remarkably, the maximum yield of ClO_2 increases with many different polar co-solvents, and the maximum conversion increases from 40% in water to as high as 70% with co-solvents (Figure 14). In addition, it was found that addition of 5 mM Triton X100, a common neutral surfactant, also increases the conversion (to 76%).

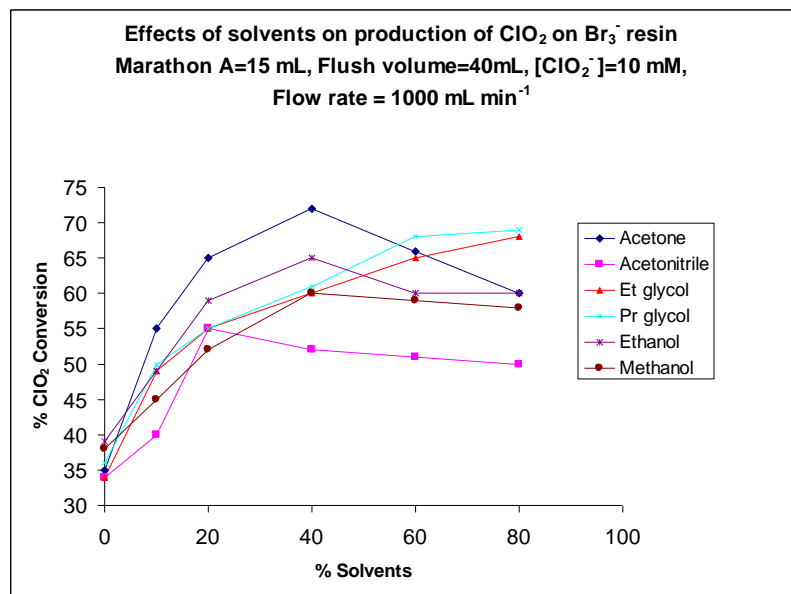


Figure 14

Maximum yield of ClO₂ with Br₃⁻ resin at different solvent compositions

Flush volume=40 mL, Volume of marathon A resin=15 mL, [ClO₂⁻]=10 mM,
Flow rate $\approx 1000 \text{ mL min}^{-1}$

Solvent	Solv Comp	Max yield of ClO ₂ (%)
Water	0%	45
Acetone	40%	72
Acetonitrile	20%	55
Ethylene glycol	80%	68
Propylene glycol	80%	69
Ethanol	40%	65
Methanol	40%	60
Triton	5 mM	76

Studies run with 10 mM chlorite using the basic model of eqs 1 and 2 show that the increased yields with cosolvents are due to increased k_{obs} values over that in water (k_{obs} increases by ~50%) as well as higher C_{max} values (e.g., from 0.4 for water to 0.84 for 80% ethanol). Thus the physical properties of the solvent, such as viscosity, may increase yields due to mass transport considerations. In addition, the increased k_{obs} values may be due to more rapid bromine dissociation and/or a faster reaction with chlorite. An examination of the dependence on chlorite feed with 40% acetone (up to 50 mM chlorite, see Figure 15) shows the usual linear dependence and flow rate dependence (Figure 16). We are currently investigating reasons for the increased conversions through more complete kinetic studies.

On the other hand, the effect of 5 mM Triton X100 is modeled by simply increasing the C_{max} value over that for pure water. The rate coefficient does not change, as would be expected since only a small quantity of Triton is added.

These results are promising since cosolvents and additives can be useful in promoting agent dissolution in decon applications. In addition, it is noted that ClO₂ effluent concentrations >30 mM are readily achieved with many co-solvent compositions.

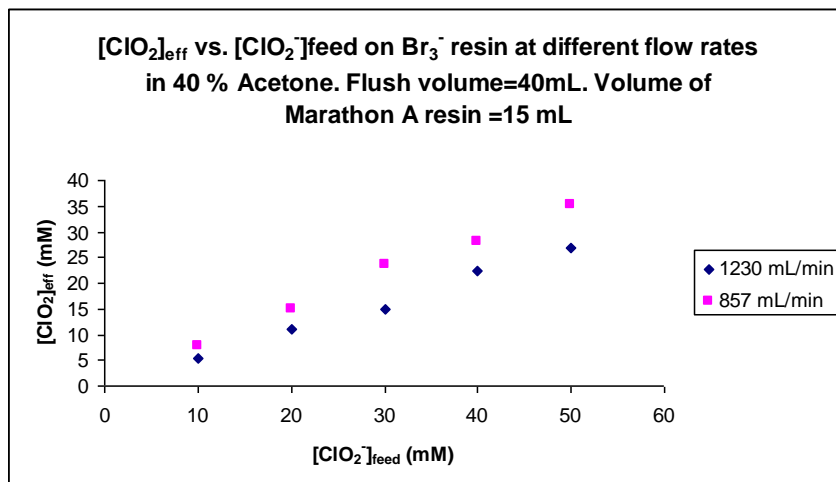


Figure 15

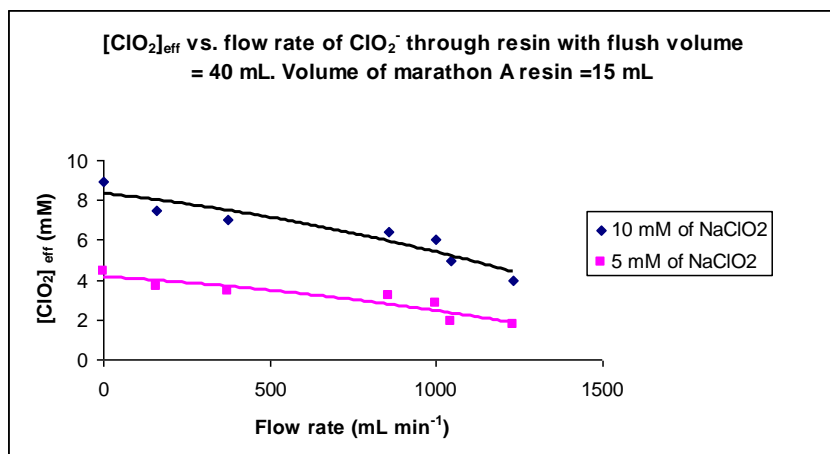


Figure 16 Dependence of chlorine dioxide yield on flow rate with 40% acetone

Ionic strength. We investigated the possible effects of varying ionic strength on ClO₂ yields using added NaF in the feed solutions and found no significant effect.

Buffering. We studied the effect of buffering (phosphate) the feed solution to pH 7 as opposed to using unbuffered purified chlorite solutions. No significant effect on ClO₂ yields was observed.

Polymeric thickeners. We have shown that polyacrylate thickeners can be use with ClO₂ solutions to produce decon solutions that cling well to vertical surfaces, enhancing exposure time. However, the thickener must be added after production of ClO₂ since the polymer solution does not flow rapidly through a resin bed.

Task 4: Selection of optimal resin/precursor solution combination through assessment of product solution and simulant testing

Oxidation of the HD stimulant CEES by ClO_2 was characterized in order to guide development optimal formulations and devices. In work not supported under this grant we have determined the likely mechanism of sulfide oxidations, and that mechanism is still under investigation. This knowledge was applied to compare CEES to other sulfides and predict the rate of reaction with HD. A high reaction rate was predicted.

Task 5: Production of a prototype sprayer device based on the most effective formulations

Example of device design parameters. Modest estimates suggest that 1 L of 20 mM chlorite can be converted to 5 mM ClO_2 in 1 min using 40 mL of Br_3^- resin. By adjusting the parameters in eq 3, the rate of effluent release and/or conversion can be increased, for example by increasing the reactor volume V . The maximum conversion can be achieved with larger reactor volumes, with $[\text{ClO}_2]$ increasing to ~10 mM in the example if V is increased substantially.

We also developed a gravity fed method to provide reproducible lab scale generation for agent testing.

Specific results for Task 5

Prototype binary sprayer

We have constructed a prototype liquid-resin binary sprayer by modification of a commercial fire extinguisher (Figure 17). A cartridge constructed of PEEK with polyethylene frits contains the modified resin and is fitted to the sprayer valve. The precursor solution (e.g., aqueous chlorite) is pressurized with nitrogen (to ~60-80 psi) in the bottle. With typical resins, the 500 mL capacity is expelled in 15 s or less through the resin. Highly concentrated aqueous ClO_2 is produced by this device.

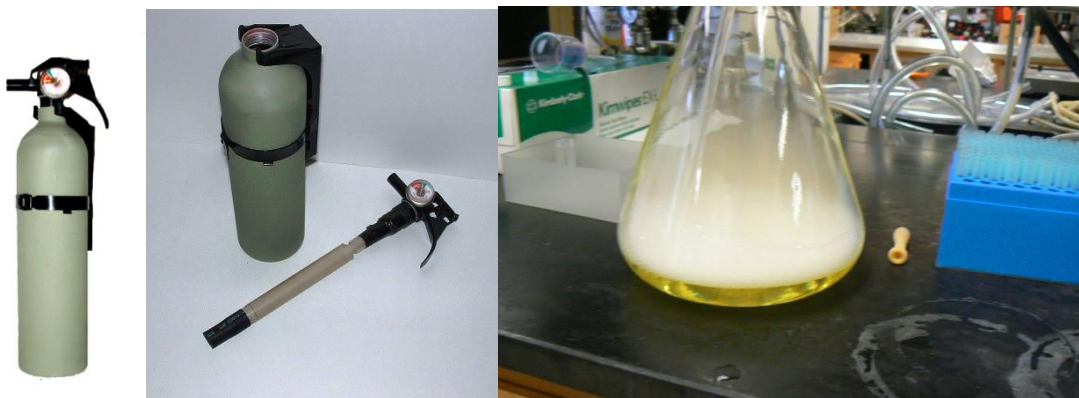


Figure 17. A functional prototype binary sprayer based on a pressurized commercial fire extinguisher. The middle figure shows the internal PEEK resin cartridge. The precursor solution (e.g., aqueous chlorite) is pressurized with

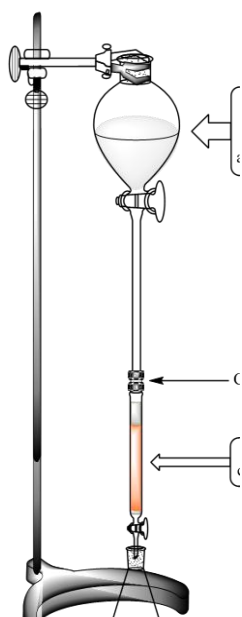
nitrogen (to ~60-80 psi) in the bottle. With typical resins, the 500 mL capacity is expelled in 15-30 s through the resin. An example of the output of the sprayer, with Triton additive that results in some foaming, is shown at right. The yellow-green color is the result of concentrated ClO_2 (the precursor solution is colorless).

In addition to this form factor, devices can be designed to deliver small quantities (e.g., a binary syringe for water purification) or a large pressurized vessel delivering many liters of decon fluid.

Preliminary studies on a small syringe generator design to allow production of mL quantities of ClO_2 solutions have been undertaken. These devices consist of a standard syringe with a resin bed cartridge attached to the fitting. It is possible to ship these components separately and then assemble for testing. However, consistent production of ClO_2 solutions by this method is not possible due to variable flow rates that occur with manual activation. We therefore developed a more reproducible gravity fed generator for use in agent testing, as described in the next section.

Gravity Fed Generator Design and Performance

The goal of this work was to produce a device based on COTS glassware that can be used on the benchtop scale to produce ClO_2 solutions at high concentration (20mM or higher) and with reproducible side product contents. The figure below shows a typical version of the simple device. Using a standard configuration, we have tested the dependence of the effluent composition on various factors, as described below. This device was used by Battelle to produce test solutions for agent testing.



Gravity Flow Generator – Solvent Selection

The method can be used to produce concentrations of ClO_2 of ~1000 ppm to ~5000 ppm depending on the co-solvent used for elution. As an example, we have used 100% methanol as the solvent. See Figure 18 below.

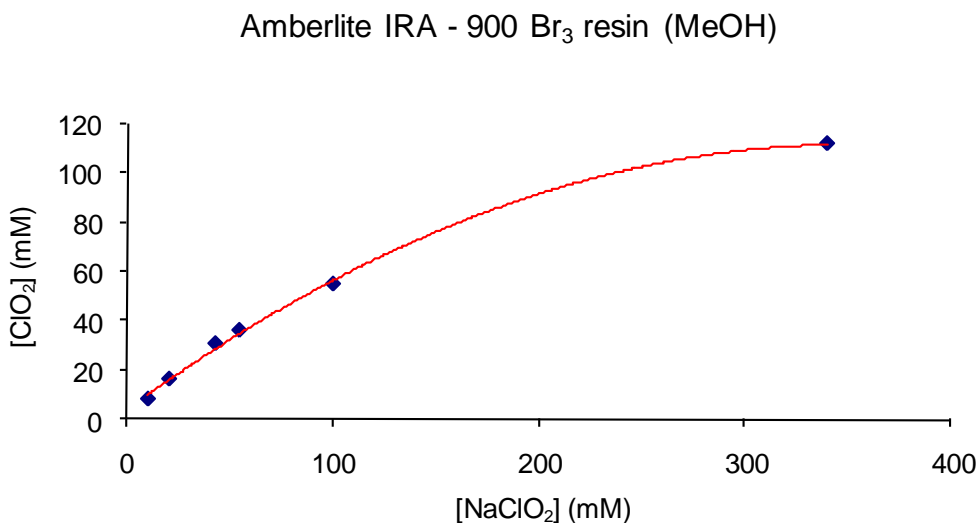
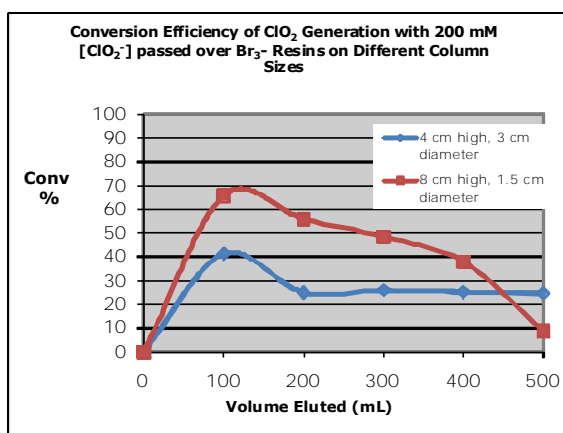
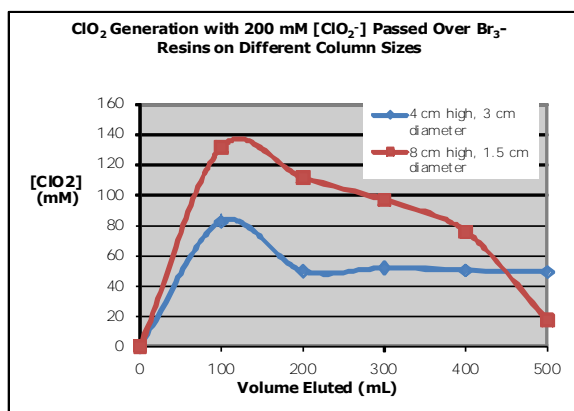
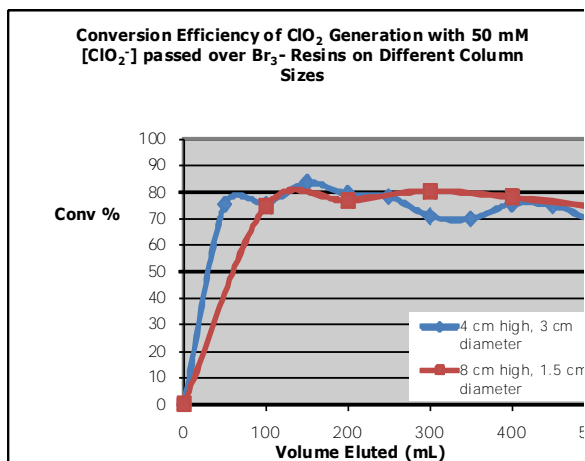
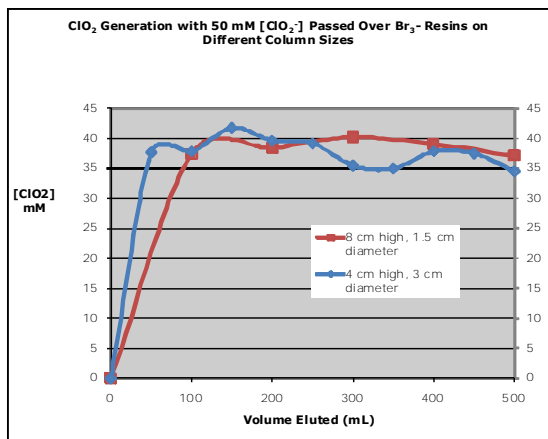


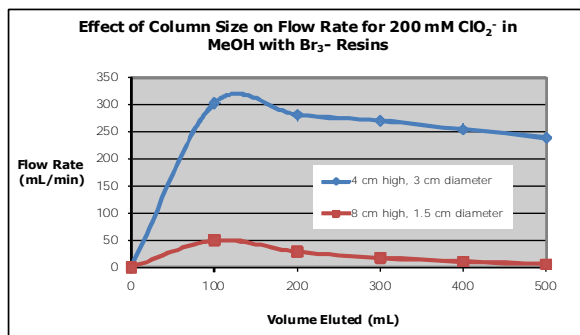
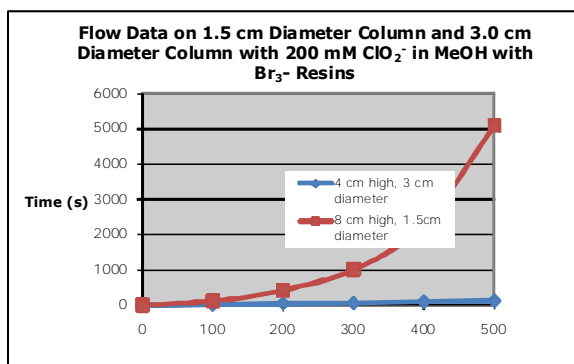
Figure 18. Performance with methanol elution showing very high ClO_2 production.

Effects of Cartridge Dimensions on Chlorine Dioxide Production/Flow Rate

The figures below show some data on ClO_2 generation (concentrations and conversion %) at 50 mM and 200 mM chlorite feed in 100% methanol. In these figures, a 4 cm H/3 cm ID and a 8 cm H/1.5 cm ID cartridge are compared. For the lower concentration feed, conversion efficiencies are typically in the 70-80% range for both cartridge dimensions. However, at 200 mM feed, the longer column (8 cm) is clearly more effective. This is readily explained by residence time differences (=cartridge volume/flow rate) for the two columns.

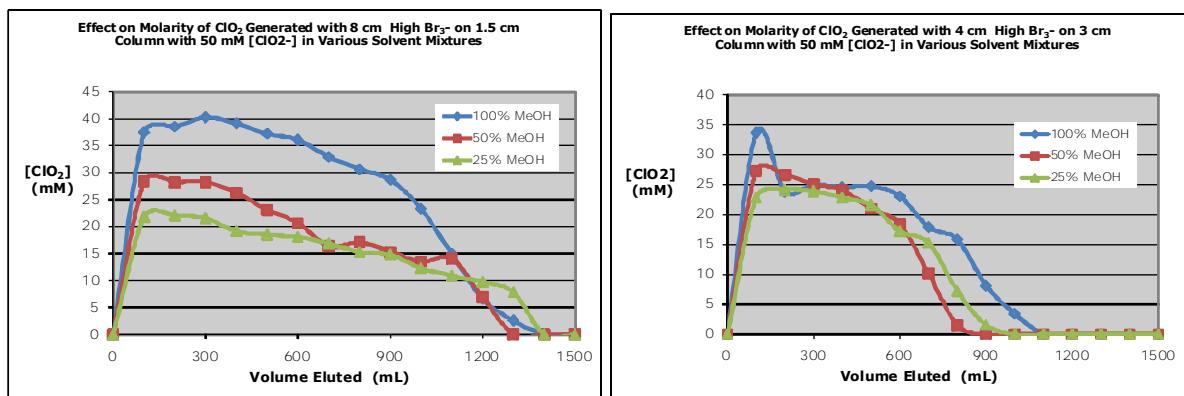


As can be seen in the charts below, the flow rate is much lower for the 8 cm cartridge, increasing residence time and conversion. For the less concentrated feed, residence time is adequate in both cases to yield high conversion efficiency.



Solvent dependence study

The effect of solvent composition is illustrated below for two different column dimensions. The use of 100% methanol significantly enhances chlorine dioxide yields in the 8 cm column.



Task 6: Agent Testing

Battelle HD and VX Decon Efficacy Studies (Report in Appendix)

Agent studies were conducted by Battelle Labs and showed that high test ClO_2 has rapid decon rates and high capacity when the formulation is supplemented with high concentrations of chlorite. The activity exceeds that of the bleach control. These studies showed that practical, rapid, and high capacity decon formulations can be produced using generated $\text{ClO}_2/\text{ClO}_2^-$ mixtures. The only significant deficiency in the testing was the capacity for VX decon was not sufficient under standard challenge conditions, although destruction of >90% was observed. Future studies should seek to determine the kinetic origin of the chlorite effect, which serves as the ultimate source of oxidizing equivalents but has low initial reactivity with agent in the absence of chlorine dioxide. In some cases, chlorine dioxide forms slowly from chlorite solutions through either acid release or a radical chain reaction that we observed at neutral pH.

Task 7: Final Report

This document.

Appendix. Battelle Report follows this page.

**Summary
Test Report**

For

**Liquid Chlorine Dioxide
Stirred Reactor Testing**

Prepared By:

1/8/2010

Adam Judd


Brian Blackstone

Hazardous Materials Research Center

Battelle

505 King Ave.

Columbus, OH 43201



DISCLAIMER

This is a work prepared for the United States Government by Battelle. In no event shall either the United States or Battelle have any responsibility or liability for any consequences of any use, misuse, inability to use, or reliance upon the information contained herein, nor does either warrant or otherwise represent in any way the accuracy, efficacy, or applicability of the contents thereof. Battelle and the United States Government do not explicitly or implicitly endorse any of the manufacturers or products discussed in this document.

TABLE OF CONTENTS

TABLES	iii
APPENDICES	iii
1.0 Introduction	4
1.1 Background	4
1.2 Objective	4
1.3 Limitations	4
1.4 Expected Use of Results.....	5
2.0 Approach.....	5
2.1 Overview.....	5
2.2 Materials and Equipment	5
2.2.1 Chemical Agents.....	5
2.2.2 Decontaminants.....	6
2.2.3 Materials.....	6
2.3 Test Matrix	6
3.0 Procedures.....	7
3.1 Method Validation.....	7
3.2 Decon Kinetics	7
4.0 Results and Analysis	10
4.1 HD Testing.....	10
4.2 VX Testing.....	12
5.0 Conclusion	14

TABLES

Table 1. Decontamination Stirred Reactor Test Matrix (HD).....	8
Table 2. Decontamination Stirred Reactor Test Matrix (VX).....	9
Table 3. HD Concentrations (ug/ml) at Selected Points.....	10
Table 4. Decontamination Efficacy (% Destroyed) vs. HD at Selected Time Points.....	11
Table 5. HD Reaction Byproducts.....	11
Table 6. VX Concentrations (ug/ml) at Selected Time Points	12
Table 7. Decontamination Efficacy (% Destroyed) vs. VX at Selected Time Points	12
Table 8. VX Reaction Byproducts.....	13

APPENDICES

APPENDIX A: Standard Operating Procedures for Portable Decontamination Device

1.0 INTRODUCTION

1.1 BACKGROUND

The Army Research Office (ARO) and the Defense Threat Remediation Agency (DTRA) are sponsoring the development of a high-capacity chlorine dioxide [ClO_2 , Chemical Abstracts Services (CAS) # 10049-04-4] decontaminant that has demonstrated efficacy on chemical agent simulants. The research team, located at the University of Florida, is interested in determining the efficacy of this developmental decontaminant against neat chemical warfare agents, specifically the vesicant distilled mustard (HD) and the nerve agent VX (VX).

1.2 OBJECTIVE

The objective of this project is to evaluate the efficacy of the developmental ClO_2 decontaminant using stirred reactor decontamination to test it against the chemical warfare agents HD and VX, as well as to characterize the byproducts of the reactions.

1.3 LIMITATIONS

Decontaminant. This testing was conducted under controlled laboratory conditions. The use of decontaminants in the field may involve different use scenarios. The method of the decontaminant's generation has not been hardened for field use and relies on a laboratory-based protocol.

Funding Level. The prime contract for this effort was funded as part of a Defense Threat Reduction Agency Broad Agency Announcement (DTRA BAA). Limited funding exists for chemical agent testing. In accordance with direction from Dr. Richardson, University of Florida, the HD work described below was given priority. Sufficient funding remained to conduct VX testing and conduct a rudimentary assessment of VX reaction byproducts.

Schedule. To meet the target price for this effort (Dr. David Richardson, University of Florida – email communication), Battelle leveraged the set-up, safety analysis, dry run, and workplace monitoring conducted for a stirred reactor decontamination effort funded by another agency. The ClO_2 testing began immediately after the conclusion of the other effort.

Byproduct Analysis. HD oxidation reaction byproducts analysis was performed with the analytical instrumentation onsite at Battelle's Hazardous Materials Research Center (HMRC). The HMRC does not have reference standards readily available for the possible reaction byproducts.

Typical VX reaction byproducts produced from oxidative systems require analytical systems (primarily liquid chromatography-mass spectrometry) that are not onsite at the HMRC. Battelle has the capability to analyze VX decontamination byproduct samples at its King Avenue location, but not within the

customer's target price provided. Therefore, a complete analysis of VX byproducts is not included within this report. For VX, only the amount of agent remaining over time and byproducts determined using Gas Chromatography/Mass Selective Detection (GC-MSD) analysis are reported here.

1.4 EXPECTED USE OF RESULTS

The results of the stirred-reactor test will be used to establish the relative effectiveness of the ClO_2 against HD and VX under stirred-reactor conditions. As the product matures through its development cycle, results will provide valuable kinetic data to be the basis for further decontaminant formulation work as the product matures.

2.0 APPROACH

2.1 OVERVIEW

One of the most fundamental tests of a decontaminant's performance is a chemical kinetics test. In its simplest form, the test determines the time it takes for a decontaminant to neutralize chemical agent in a reaction vessel. The testing can also be coupled with additional testing to determine reaction byproducts. This will provide additional information to develop health-based assessments related to residual hazards that may remain after decontamination.

Testing uses a simple stirred reactor consisting of a glass reaction vessel and a stir device. As requested by the client, the liquid decontaminant and agent were mixed in approximately a 111:1 volume ratio and allowed to react. Aliquots of the mixture were removed at fixed time points, the reaction was quenched immediately, and the agent/decontaminant mixture was extracted and analyzed for remaining agent using a GC-MSD.

Kinetics testing methodology is appropriate for liquid decontaminants such as bleach, hydrogen peroxide, decontamination solution number 2 (DS-2), and other developmental formulations such as the "high-test" liquid ClO_2 —the centerpiece of this effort. The "high-test" ClO_2 was generated by passing chlorite solution through a functionalized resin bed to form ClO_2 in the effluent. This proprietary process was performed on the bench top, providing ample liquid decontaminant for kinetics testing.

2.2 MATERIALS AND EQUIPMENT

2.2.1 CHEMICAL AGENTS

This test included the chemical agents HD (CAS# 505-60-2) and VX (CAS# 50782-69-9). DTRA previously procured sufficient quantities of both agents. The Edgewood Chemical Biological Center (ECBC) approved transfer of agent for use on this project within the limitations of Battelle's bailment

agreement. The chemical agent purity was measured previously and is reported below. Volume additions were not adjusted for agent purity, but theoretical time-zero concentrations were corrected based on agent purity.

2.2.2 DECONTAMINANTS

The ClO_2 solution was generated using a simple combination of a column and a reservoir flowing under gravity only. The production of ClO_2 used a bromine-modified resin and a precursor solution of sodium chlorite (NaClO_2 , CAS# 7758-19-2, concentration ~50 mM). The precursor solution was passed through a bed of the resin, and ClO_2 was produced in the effluent. The conversion is on the order of 30 to 60%, depending on the solvent (the highest conversions are with methanol solvent and the lowest are with pure water). Methanol was used as the solvent in this testing. Therefore, the maximum concentration of ClO_2 was on the order of 10 to 30 mM. These are very high concentrations, and the levels were chosen to maximize rates of reaction with sulfides. The actual concentration of the ClO_2 was determined using a portable UV spectrophotometer from Ocean Optics and measuring the absorbance at 359 nm. Appendix A provides a detailed method for producing the ClO_2 solution.

2.2.3 MATERIALS

Testing used the following materials:

- Multi-position stir plate
- 1-L flask with stopcock
- Glass column (1.5-cm diameter)
- Bromine-modified resin
- Sodium chlorite
- Methanol
- 25-ml flasks
- Teflon stir bars
- Quenching solution
- Extraction jars
- Chloroform
- Pipets
- Gas chromatography with flame photometric detector (GC-FPD) and/or gas chromatography-mass spectrometry (GC-MS).
- UV Spectrometer

2.3 TEST MATRIX

Decontamination testing was conducted in a stirred reactor to determine the decontamination kinetics and capacity of the ClO_2 solution. Chemical agent was added to a stirred flask of decontaminant to achieve a ~111:1 decon:agent ratio. The solution was sampled over time to determine the agent concentration.

Table 1 shows the test matrix for the stirred-reactor kinetics testing. Testing included test samples and appropriate controls. Seven different decontamination or control solutions were tested:

- A. Chlorine dioxide in methanol plus water
- B. Chlorine dioxide in methanol plus sodium chlorite

- C. Sodium chlorite in methanol
- D. Water in methanol
- E. Chlorine dioxide and water in methanol - no agent control
- F. 5.25% Bleach
- G. Methanol only

3.0 PROCEDURES

3.1 METHOD VALIDATION

The reaction kinetics are determined by sampling the stirred reactor over time and measuring agent concentration. The sample collected must be quenched immediately to stop the reaction between the decontaminant and the agent. A 50- μ l sample was drawn from the stirred reactors at specified time periods. The sample was transferred to a solution containing solvent for extraction and analysis as well as a quenching solution. The decontaminants were quenched using a sufficient amount of reductant to completely reduce the remaining oxidant in the solution.

In the laboratory, the ClO_2 developer freezes the solution with liquid nitrogen to quench the reaction. A hazard analysis of the process indicates that flash-freezing is not a viable option for this chemical warfare agent (CWA) kinetic procedure. In lieu of flash-freezing, 1.5 N solution of sodium sulfite (Na_2SO_3 , CAS#7757-83-7) in pH 9 Tris buffer was selected as the quench for ClO_2 . The higher concentration (1.5 N) of sodium sulfite was selected to provide sufficient reductant in a relatively low volume of liquid. Tris was used to provide a buffered solution of sufficiently high pH to maximize the extraction efficiency for VX. This quench has been used in the HMRC with other ClO_2 -based decontaminants.

Method validation of the quenching and extraction steps indicates that greater than 95% of the HD can be recovered but only 68% of the VX. Typically, a 68% recovery would not meet the minimum recovery criteria (>80%) for stirred reactor testing. Unfortunately, in this case, sufficient resources (schedule and cost) were not available on the contract to continue with the method development so the method was accepted as described.

3.2 DECON KINETICS

A total of 10 decontamination kinetics trials were performed for each agent (ClO_2 plus various controls). The 25-ml reaction flasks with teflon stir bars were placed on a multi-position stir plate. Eleven milliliters of decon solution was added to each flask. Chemical agent (100- μ l) was added to each reaction flask. At the specified times, 50- μ L aliquots were withdrawn from each flask and transferred to a vial containing 2 ml of extraction solvent (CHCl_3 with internal standard) and quenching agent. The sample was vortexed for ~1 minute and the solvent was transferred to duplicate GC vials for GC-MS analysis. Samples were accounted for using a signed chain of custody (CoC).

Two “no decon” positive controls were prepared by adding 11 ml of methanol or 10 ml of methanol plus 1 ml water to a flask and applying 100- μ l of the respective agent. A ClO_2 negative control (blank) was prepared by adding 10 ml of the decon plus 1 ml of water to a flask. No agent was added to the blank. A test parameter control sheet (TPCS) was filled out for each trial.

Table 1. Decontamination Stirred Reactor Test Matrix (HD)

ID	Contents of 25ml Flask							Contents of 15ml Test Tube up to 60 min	Contents of 15ml Test Tube up to 60 min	Volume Taken From Flask and added to Tube up to 60 min	Contents of 15ml Test Tube at 24 hr	Contents of 15ml Test Tube at 24 hr	Expected Volume Taken From Flask and added to Tube at 24 hr	Actual Volume Taken From Flask and added to Tube at 24 hr
	Sample ID	Agent	ClO ₂	Inhibitor	DI H ₂ O	Bleach	MeOH	Quench/TRIS	CHCl ₃	Sample	Quench/TRIS	CHCl ₃	Sample	Sample
Test	1-A-1 1-A-2 1-A-3	100ul	10ml		1ml			1ml	2ml	50UL	1ml	2ml	10ml 6ml 6ml	5ml 6ml 6ml
Test	1-B-1 1-B-2	100ul	10ml	1mL				1ml	2ml	50UL	1ml	2ml	10ml	6ml
Control	1-C-1	100ul		1mL			10ml	1ml	2ml	50UL	1ml	2ml	10ml	9ml
Control	1-D-1	100ul			1ml		10ml	1ml	2ml	50UL	1ml	2ml	10ml	10ml
Control*	1-E-1		10ml		1ml			1ml	2ml	50UL	1ml	2ml	10ml	5ml
Post Spike	1-E-1-PS							1ml	2ml	50UL	NA	NA	NA	NA
Control	1-F-1	100ul				11ml		1ml	2ml	50ul	1ml	2ml	10ml	9ml
Control	1-G-1	100ul					11ml	1ml	2ml	50ul	1ml	2ml	50ul**	50ul

Table 2. Decontamination Stirred Reactor Test Matrix (VX)

ID	Contents of 25ml Flask							Contents of 15ml Test Tube up to 60 min	Contents of 15ml Test Tube up to 60 min	Volume Taken From Flask and added to Tube up to 60 min	Contents of 15ml Test Tube at 24 hr	Contents of 15ml Test Tube at 24 hr	Expected Volume Taken From Flask and added to Tube at 24 hr	Actual Volume Taken From Flask and added to Tube at 24 hr
	Sample ID	Agent	ClO ₂	Inhibitor	DI H ₂ O	Bleach	MeOH	Quench/TRIS	CHCl ₃	Sample	Quench/TRIS	CHCl ₃	Sample	Sample
Test	1-A-1 1-A-2 1-A-3	100ul	10ml		1ml			1ml	2ml	50UL	1ml	2ml	215ul 215ul 215ul	
Test	1-B-1 1-B-2	100ul	10ml	1mL				1ml	2ml	50UL	1ml	2ml	215ul 215ul	
Control	1-C-1	100ul		1mL			10ml	1ml	2ml	50UL	1ml	2ml	215ul	
Control	1-D-1	100ul			1ml		10ml	1ml	2ml	50UL	1ml	2ml	215ul	
Control*	1-E-1		10ml		1ml			1ml	2ml	50UL	1ml	2ml	215ul	
Post Spike	1-E-1-PS							1ml	2ml	50UL	NA	NA	NA	NA
Control	1-F-1	100ul				11ml		1ml	2ml	50ul	1ml	2ml	215ul	
Control	1-G-1	100ul					11ml	1ml	2ml	50ul	1ml	2ml	215ul	

4.0 RESULTS AND ANALYSIS

4.1 HD TESTING

Table 3 contains the HD concentrations ($\mu\text{g/ml}$) in the stirred reactors at the various time points for the decontaminants and controls tested. Given the volume, concentration, and purity of the HD used to spike the reactor, the initial agent concentration in the reactor flask was approximately 11,137 $\mu\text{g HD/ml}$ solution as calculated in equation (1).

$$\text{Init Conc} = C * D * P / V \quad (1)$$

Where

C	=	Concentration of HD
D	=	Density of HD
P	=	Purity of HD
V	=	Volume of the total solution

$$\begin{aligned} \text{Init Conc} &= 100 \mu\text{l HD}/11.1 \text{ ml soln} * 1 \text{ ml HD}/10^3 \mu\text{l} * 1.268 \text{ g HD/ml} * 10^6 \mu\text{g HD/g} * 0.975 \text{ (purity)} \\ &= \underline{11,137 \mu\text{g HD/ml}} \end{aligned}$$

The concentration of the chlorine dioxide used for the HD testing as determined using a spectrophotometer was 18.96 mM.

Table 3. HD Concentrations ($\mu\text{g/ml}$) at Selected Time Points.

Time	ClO_2	ClO_2	ClO_2	$\text{ClO}_2 + \text{NaClO}_2$	$\text{ClO}_2 + \text{NaClO}_2$	NaClO_2	Bleach	No VX	MeOH	MeOH+ H_2O
2	10,264	9,384	10,520	<40	<40	11,928	3,340	<40	11,392	10,456
5	10,152	10,192	20,160	<40	<40	12,096	165	<40	11,136	10,344
10	11,280	10,528	19,128	<40	<40	12,264	<40	<40	10,624	10,112
15	9,856	10,528	20,808	<40	<40	11,552	<40	<40	11,328	9,912
30	10,568	10,152	19,168	<40	<40	11,400	<40	<40	10,560	9,944
60	10,032	9,376	19,464	<40	<40	8,416	<40	<40	10,496	9,680

Note: Samples were taken for a 24-hour time point but the data was deemed unreliable. The reactor flasks were not covered during the time period and considerable evaporation occurred over time. The rate of evaporation was not consistent between flasks.

Decontamination efficacy was calculated as percent of agent destroyed as shown in Equations (2) and (3).

$$\text{Eff (t)} = \{1 - (\text{Conc(t)}/\text{Init Conc})\} * 100\% \quad (2)$$

Where

Eff	=	Efficacy (%)
t	=	Time interval (2, 10, 15, 30, and 60 min)
conc(t)	=	Concentration at time (t)
Init Conc	=	Initial concentration (11,137 $\mu\text{g/ml}$)

$$\text{Conc (t)} = C * D \quad (3)$$

Where:

Conc (t) = Concentration in flask at time
C = Concentration identified by GC-MS (ng/ml)
D = Dilution factor {40 (2 ml extraction volume/50 µl sample aliquot)}

Table 4 contains the decontamination efficacy results for the three test solutions and the bleach control.

Table 4. Decontamination Efficacy (% Destroyed) vs. HD at Selected Time Points

Time	ClO ₂	ClO ₂	ClO ₂	ClO ₂ + NaClO ₂	ClO ₂ + NaClO ₂	NaClO ₂	Bleach
2	7.8%	15.7%	5.4%	>99.6	>99.6	See Note 1	70.0%
5	8.8%	8.5%	See Note 1	>99.6	>99.6	See Note 1	98.5%
10	See Note 1	5.5%	See Note 1	>99.6	>99.6	See Note 1	>99.6
15	11.5%	5.5%	See Note 1	>99.6	>99.6	See Note 1	>99.6
30	5.1%	8.8%	See Note 1	>99.6	>99.6	See Note 1	>99.6
60	9.9%	15.8%	See Note 1	>99.6	>99.6	24.3%	>99.6

Note 1. Negative values due to the accepted error range in gas chromatography measurements.

For the chlorine dioxide containing samples, mass spectra were analyzed to determine potential reaction byproducts for HD (see Table 5). Byproducts were identified by reference matching, using the National Institute of Standards and Technology (NIST) 2000 mass spectral library. The library contains spectra for common HD oxidation products. Table 5 contains the byproducts identified for the HD reactions.

Table 5. HD Reaction Byproducts

Compound	Samples	~ Retention Time
Divinyl sulfone	ClO ₂ + NaClO ₂	5.25
1-(2-chloroethyl)thio-2-methoxyethane	ClO ₂	5.81
2-chloroethyl vinyl sulfoxide	ClO ₂	6.6
	ClO ₂ + NaClO ₂	
Bis(2-chloroethyl) disulfide	ClO ₂	8.08
	ClO ₂ + NaClO ₂	
	NaClO ₂ only	
Bis(chloroethyl) sulfone	ClO ₂ + NaClO ₂	8.71
	NaClO ₂ only	
1,4-Dithiane-1-oxide	ClO ₂	8.86
	NaClO ₂ only	
Bis(chloroethyl) sulfoxide	ClO ₂	8.94
	ClO ₂ + NaClO ₂	
	NaClO ₂ only	

The stirred reactor results indicate that there is very little decontamination efficacy for the ClO_2 /methanol solution against HD. When sodium chlorite is added to the ClO_2 /methanol solution, rapid destruction of the HD occurs within the first two minutes. This is much quicker than the bleach control and other oxidative systems that Battelle has tested in the past including hydrogen peroxide and peroxymonosulfate. The reaction products identified for the ClO_2 /methanol/ NaClO_2 reactions are similar to those seen with other oxidative systems. Sodium chlorite in methanol-only does not appear to be effective against HD.

4.2 VX TESTING

Table 6 contains the VX concentrations ($\mu\text{g}/\text{ml}$) in the stirred reactors at the various time points for the decontaminants and controls tested. Given the volume, concentration, and purity of the VX used to spike the reactor, the initial agent concentration was approximately 8811 μg VX/ml solution as calculated in equation (1).

$$\begin{aligned} \text{Init Conc} &= 100 \mu\text{l VX}/11.1 \text{ ml soln} * 1 \text{ ml VX}/10^3 \mu\text{l} * 1.0083 \text{ g VX}/\text{ml} * 10^6 \mu\text{g VX}/\text{g} * 0.970 (\text{purity}) \\ &= \underline{8811 \mu\text{g VX}/\text{ml}} \end{aligned}$$

The concentration of the chlorine dioxide used for the VX testing as determined using a spectrophotometer was 26.64 mM.

Table 6. VX Concentrations ($\mu\text{g}/\text{ml}$) at Selected Time Points.

Time	ClO_2	ClO_2	ClO_2	$\text{ClO}_2 + \text{NaClO}_2$	$\text{ClO}_2 + \text{NaClO}_2$	NaClO_2	Bleach	No VX	MeOH	MeOH+ H_2O
2	5456	4496	5240	675.6	645.6	7336	8772	0	9620	8772
5	5616	4688	5256	575.2	493.6	428	<40	0	9320	6228
10	4648	4392	4384	546	429.2	457.6	<40	0	8764	10232
15	4816	9152	4000	496.8	387.6	388	<40	0	9212	10560
30	4384	4256	5576	431.2	268.4	305.2	<40	0	9136	8252
60	4856	5480	4000	349.2	271.6	228.4	<40	0	10028	7000

Decontamination efficacy was calculated as percent of agent destroyed using equation (2). Table 7 contains the decontamination efficacy results for the three test solutions and the bleach control.

Table 7. Decontamination Efficacy (% Destroyed) vs. VX at Selected Time Points

Time	ClO_2	ClO_2	ClO_2	$\text{ClO}_2 + \text{NaClO}_2$	$\text{ClO}_2 + \text{NaClO}_2$	NaClO_2	Bleach
2	38.1%	49.0%	40.5%	92.3%	92.7%	16.7%	0.4%
5	36.3%	46.8%	40.3%	93.5%	94.4%	95.1%	>99.5%
10	47.2%	50.2%	50.2%	93.8%	95.1%	94.8%	>99.5%
15	45.3%	See Note 1	54.6%	94.4%	95.6%	95.6%	>99.5%
30	50.2%	51.7%	36.7%	95.1%	97.0%	96.5%	>99.5%
60	44.9%	37.8%	54.6%	96.0%	96.9%	97.4%	>99.5%

Note 1. Negative values due to the accepted error range in gas chromatography measurements. It is not clear as to why the data for the 15 minute time point are significantly different from the other time points.

For the chlorine dioxide containing samples, mass spectra were analyzed to determine potential reaction byproducts for VX (see Table 8). Byproducts were identified by reference matching using the NIST 2000 mass spectral library. The library contains spectra for a select number of VX degradation products. The major degradation products of VX, S-2-(diisopropylaminoethyl)-methylphosphonothioic acid (EA2192), ethyl methylphosphonic acid (EMPA), and methylphosphonic acid (MPA) are not detected using gas chromatography.

Table 8. VX Reaction Byproducts

Compound	Samples	~ Retention Time
Ethyl methyl methylphosphonate	ClO ₂	4.39
	ClO ₂ + NaClO ₂	
	NaClO ₂ only	
N,N-Diisopropylformamide	ClO ₂	5.08
	ClO ₂ + NaClO ₂	
	NaClO ₂ only	
Diethyl dimethylpyrophosphonate	ClO ₂	8.12

The stirred reactor results indicate that there is some decontamination efficacy for the ClO₂/methanol solution against VX. The efficacy does not exceed approximately 40-50%, potentially indicating a capacity issue with the ClO₂/methanol solution. Recall that the extraction efficiency for VX was only 68%. Therefore the actual decontamination efficacy may be overestimated due to the poor sample recovery efficiency.

When sodium chlorite is added to the ClO₂/methanol solution, rapid destruction of the VX occurs within the first two minutes but the reaction does not go to completion even after 60 minutes. This is also thought to be a capacity issue. Typically, 10-20 molar equivalents of oxidant are required to react with one mole of VX. Given that sodium chlorite can regenerate ClO₂ in solution; the actual molar concentration (capacity) of the ClO₂/methanol/NaClO₂ solution is not known.

Sodium chlorite in methanol does appear to be effective against VX presumably due to the auto-generation of ClO₂ from the reaction of the sodium chlorite with the acid initially present in the solution. Over time, the speed of the reaction appears to increase dramatically most likely due to the increased production of ClO₂ from the remaining sodium chlorite and the acid produced from VX destruction.

As with HD, the reactions are much quicker than the bleach control and other oxidative systems that Battelle has tested in the past. The reaction products that were able to be identified for the ClO₂/methanol/NaClO₂ reactions using GC/MS are similar to those seen with other oxidative systems. Unfortunately, the presence of EMPA or MPA, typical oxidation products of VX, could not be verified.

5.0 CONCLUSION

A solution of liquid chlorine dioxide and sodium chlorite in methanol appears to be effective at destroying HD and VX. Under the conditions tested, the decontamination solution reacts rapidly and form reaction byproducts similar to those seen with other strong oxidants. Reaction rates appear faster than the 5.25% bleach control and other oxidative decontaminants tested previously using similar test conditions.

APPENDIX A

Standard Operating Procedures for Portable Decontamination Device

Standard Operating Procedures for Portable Decontamination Device

Packing the Column

1. Obtain a 1.5-cm-diameter test tube that is over 8 cm in height and measures 8 cm from the bottom of the tube. Draw a line around the neck of the tube, and fill the tube to that height with the resins.
2. Invert the column and place the tube snugly into the neck of the column, such that when the column is reverted, the resins fall into the depth of the column. Wash residual resins on the sides of the column with deionized (DI) water into the base of the column.
3. Fill the column to the widening of the neck with DI water. Place one gloved hand over the end so that no water or resins can escape; invert multiple times to ensure that the resins are mixed and that there are no visible air gaps.
4. Put packing cotton or fiber in a small ball and push it down the length of the column such that it keeps the shape of the column. Approximately 1 cm should be sufficient, as long as the shape of the column is kept constant.
5. Rinse the column by running DI water through it to remove any contaminants from the packing process. Three volumes are sufficient, but ensure the water level does not go past the fiber/resins such that they dry. If drying occurs, repack the column.
6. Fill the column after rinsing to the top and clamp it to a stand or ring assembly capable of holding its weight, along with the flask and one liter of fluid. Make sure the stopcock is closed.

Assembly of Flask

1. Fill the flask with the desired amount or concentration of reagent and place it in the column's glass joint. Make sure that all stopcocks are closed, and screw down the gasket/plastic ring to create an airtight seal. Open the stopcock on the column and observe if the water stops flowing out after a vacuum is created. If the water does not stop, the seal is not airtight, and the gasket must be checked or replaced. Leave this stopcock open.

Operation of Column

1. Open the stopcock on the flask assembly to allow the reagent to enter the column reservoir. Observe the color of the liquid coming from the column; once the clear water portion passes and the reaction starts, the liquid will turn dark yellow.
2. Collect desired portion of the yellow liquid, depending on the aliquot of interest.

Decontamination of Excess Disinfectant

1. Create a stock of concentrated sodium thiosulfate pentahydrate by adding 50 g of thiosulfate to 1 L of water.
2. Gather all unwanted aliquots of disinfectant mixture and add them to a large beaker or Erlenmeyer flask. Titrate the thiosulfate into the disinfectant mixture until the color changes from yellow to clear. Allow the mixture to stand for 15 minutes before disposing of it in the sink or drain.

Images in order of appearance:

The image below shows a chlorine dioxide generation column ready for operation.

